ABSTRACT

CHEMISTRY

DYERS JR., LEON B.S. SAVANNAH STATE UNIVERSITY, 2000

DEVELOPMENT OF SALEN METAL COMPLEXES FOR THE POTENTIAL CATALYTIC USE IN ASYMMETRIC REACTIONS

Advisor: Professor Xiu (James) Bu

Thesis dated July 2005

This research effort is focused on the development of new transition-metal salen complexes bearing bulky *t*-pentyl groups to further understand their role in the directing of substrates to the reactive metal centers. These new chiral and achiral transition-metal salen complexes also possess the ability to be novel asymmetrical catalysts. A series of salen ligands were prepared by the condensation of 3,5-di-*t*-pentyl salicylaldehyde with five different diamines: (1) 1,3-diamino-propan-2-ol, (2) benzene-1,2-diamine, (3) ethylene-1,2-diamine, (4) (S,S)-1,2-diamino-1,2-diphenylethane, and (5) 1,2-diaminocyclohexane. These ligands were treated with transition metal salts to give the corresponding transition-metal salen complexes. As a result, five new systems with three crystal x-ray structures were obtained.

DEVELOPMENT OF SALEN METAL COMPLEXES FOR THE POTENTIAL CATALYTIC USE IN ASYMMETRIC REACTIONS

A THESIS

SUBMITTTED TO THE FACULTY OF CLARK ATLANTA UNIVERSITY

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BY

LEON DYERS JR.

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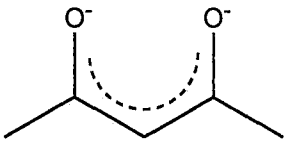
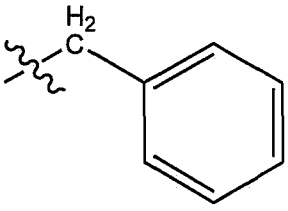
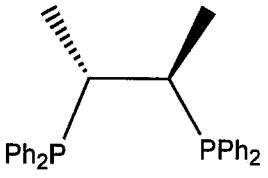
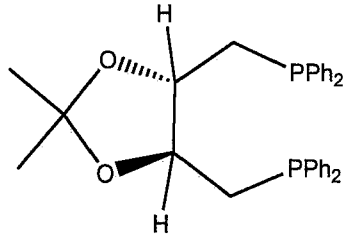
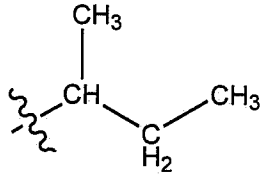
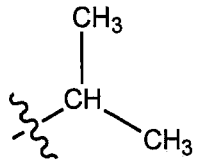
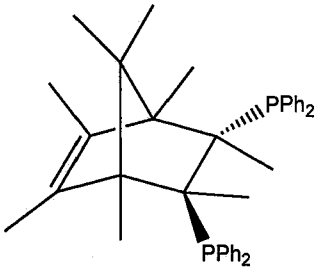
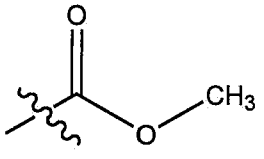
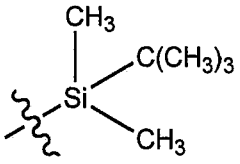
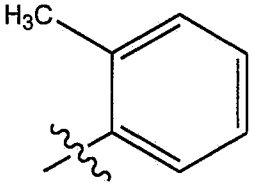
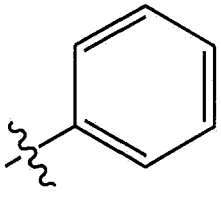
ABBREVIATIONS

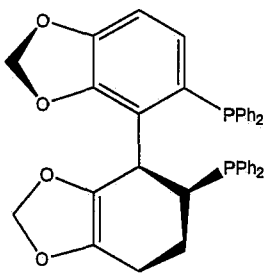
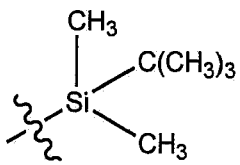
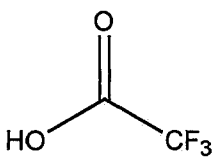
Other less common abbreviations are given in the text when the term is used.

acac	Acetylacetonate 
Anal.	analytically
Bn	Benzyl 
Calcd.	calculated
Chiraphos	2*R*,3*R*(+)-bis(diphenylphosphino)butane 
^{13}C-NMR	Carbon 13 Nuclear Magnetic Resonance
d	doublet
D	dextro

% de	% Diastereomeric excess	
DIOP	DiisooctylPhthalate	
% ee	% Enantiomeric excess	
EI-MS	Electron Ionization Mass Spectroscopy	
Equiv	Equivalents	
ESR	Electron Spin Resonance	
Et	Ethyl	$-CH_2CH_3$
FT-IR	Fourier Transfer Infrared Spectroscopy	
g	gram	
h	hours	
^{1} H-NMR	Proton Nuclear Magnetic Resonance	
i-Bu	Isobutyl	

i-Pr	Isopropyl	
L	Levo	
m	multiplet	
Me	Methyl	$-CH_3$
mmol	millimoles	
mol	moles	
MS	Molecular Sieves	
n-Bn	Butyl	$-(CH_2)_3CH_3$
Norphos	*R*(+)-bis(diphenylphosphino)binaphthyl	
n-Pr	Propyl	$-(CH_2)_2CH_3$
OAc	Acetate	

o-Silyl	Ortho-Silyl	
OTf	Trifate	$-O(O_2)S\ CF_3$
o-Tolyl	Ortho-Tolyl	
Ph	Phenyl	
ppm	parts per million	
q	quartet	
R	rectus	
ri/re	top face	
r.t.	room temperature	
s	singlet	
S	sinister	

si	bottom Face	
(S)-SEGPHOS	(4,4'-bi-1,3-benezodioxole)-5,5'-diyl-bis-(dipheneyl-phosphine)	
TBSO	*tert*- Butyldimethylsilyloxy	
TFA	Trifluoroacetic Acid	
TLC	Thin Layer Chromatography	
TMS	Trimethylsilane	$SiH(CH_3)_3$
t	triplet	
UV	Ultra Violet Spectroscopy	

CHAPTER I

INTRODUCTION

Pasteur's landmark revelation of the molecular origins of optical activity is evident in the research of many scientists today, but unlike Pasteur, scientists today more than just rationalize observable chiral phenomena. Today's chemists are interested and engaged in designing and synthesizing molecular substrates that display specific properties, activities, and functions.[1] This realm of optically active molecules includes the endless list of therapeutic agents, vitamins, proteins, peptides, and other complex molecules.

In nature, the synthesis of optically active substrates is usually carried out by enzyme catalysis. This catalysis gives such exceptional optical yields that chemists have used them for many years, but they usually require very long reaction times, and the isolated yields are typically low. Secondly, enzymes are generally very large, yet fragile molecules susceptible to slight physical changes in environment. Also, enzymes might not display the same enzymatic activity with different derivatives of a class of substrates. Thus, other complementary methods capable of producing enantiomerically pure compounds are needed.

Organometallic catalysts can be easily designed, and can be easily manipulated to optimize their effectiveness. These molecules are effective with no

intolerance to the different substrate derivatives, usually exhibiting the same optical yields for a wide range of derivatives. Also, this catalysis is often very effective with nominal amounts of catalyst.

Catalytically asymmetrical synthesis is a tool that gives one the ability to produce large quantities of enantiomerically pure compounds. This is a very useful feature considering that the pharmaceutical companies and federal agencies such as the Food and Drug Administration are pushing for more enantiomerically pure active substrates in foods and medications. As stated before, even small quantities of enantioenriched catalysts have huge implications, which are being revealed with more mechanistic comprehension and chemical intuition.

Under the mentorship of Dr. Xiu R. Bu, this research group has done extensive work in the area of asymmetrical synthesis of several forms, including cyanation, epoxidation, and Diels-Alder reactions. The most recent publication in this area has been that of Sidney Liang and Xiu R. Bu,[2] where Liang explains how they synthesized the most effective catalyst for cyanation to date, giving 92-97% ee, enantimeric excess.

The current mission of this group is to develop new classes of transition metal catalysts, which could potentially serve as achiral or chiral salen catalyst. The long-term goal of this group is to evaluate these complexes in catalytic Diels-Alder reactions. This area is of particular interest because the resultant products are of pharmaceutical importance. In this thesis, the progress made by this group in the area of developing

several new series of Schiff base ligands that are furnished with *t*-pentyl steric groups is reported.

The Diels-Alder reaction is standard for the formation of a six-membered ring. In principle, it allows the formation of four asymmetrical centers, and because of this reaction's cyclic transition state arising from the suprafacial-suprafacial interaction, its relative stereochemistry is usually well defined.

The advantage of asymmetrical Diels-Alder reactions is that countless compounds, even many natural products, such as therapeutic agents, can be synthesized in the early stages of the synthetic scheme. An example of this is that of Loganine ®, which is obtained by asymmetrical synthesis in very high enantiomeric excess.[3] In creating a more selective asymmetric Diels-Alder catalyst, therapeutic agents such as Loganine ® and Indinavir, an HIV protease inhibitor, become economically feasible for the many people in dire need of them.

CHAPTER II

BACKGROUND

Asymmetrical Diels-Alder reactions were first investigated roughly three decades ago by introducing a removable chiral auxiliary on the diophene.[4-7] The use of Lewis acids (e.g., $AlCl_3$) to catalyze the Diels-Alder reaction was a great development which allowed this reaction to be run in very mild conditions, often below 0 °C. [8-9] The coordination of the Lewis acid with the carbonyl groups on the dienophile allowed this activation process to take place. The mild conditions of this reaction resulted in high levels of diastereomeric excess (<95%) with menthyl fumarate or menthyl acrylate and a diene.[10-11]

The first successful asymmetric catalyzed Diels-Alder reaction was by Koga et al.[12] in 1979. This group used a menthoxydichloroaluminum catalyst to perform the cycloaddition of methacrolein to cyclopentadiene (Figure 1). As a follow up, Koga et al. published another paper in 1987 that confirmed the results (57% ee) for the cycloadduct I and proposed an explanation based on the observed absolute configuration.[13]

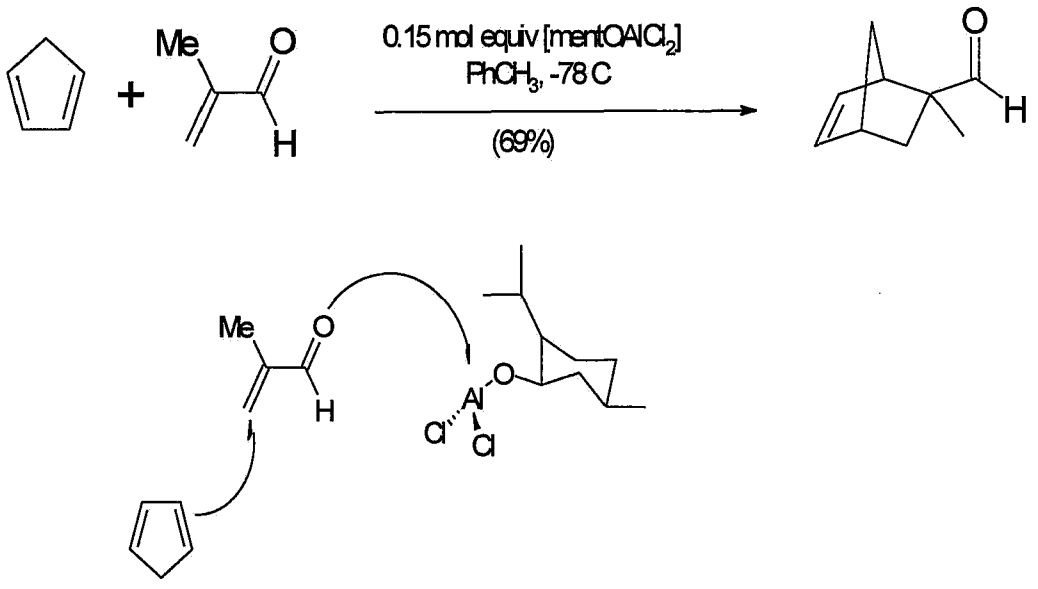


Figure 1. Proposed chiral aluminum catalyst for the cycloaddition of methacrolein on cyclopentadiene by Koga et al.[12]

In a review of chiral aluminum catalysts, one finds that various dialkoxychloroaluminum complexes were studied by Herrmann et al.,[14] who also studied the effects of time on the composition of the catalytic solution using Al NMR and cryoscopic measurements, which eventually revealed the fast formation of the dimeric form of the complex at room temperature from the monomer. It was discovered that this rapid formation slowed down in the presence of a dienophile like methyl acrylate.

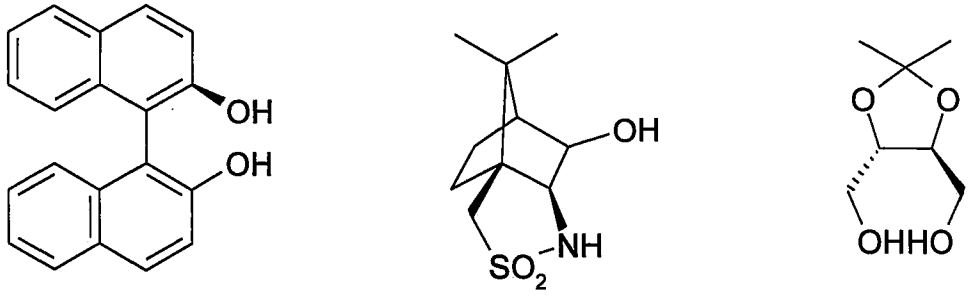


Figure 2. Some examples of the many bidentate ligands thoroughly investigated in catalytic Diels-Alder reactions via Herrmann et al.'s methodology. [14]

This methodology allowed many researchers to study the catalytic Diels-Alder reaction between methyl acrylate and cyclopentadiene for the different catalytic species. When this was done, they found that the monomeric species were the best. Several chiral bidentate ligands, a few examples are shown in Figure 2, were studied and documented with ee's achieved up to 70%.

Chiral aluminum complexes derived from bis-sulfnamides with C_2 symmetry were prepared by Corey et al. (Figure 3).[15]

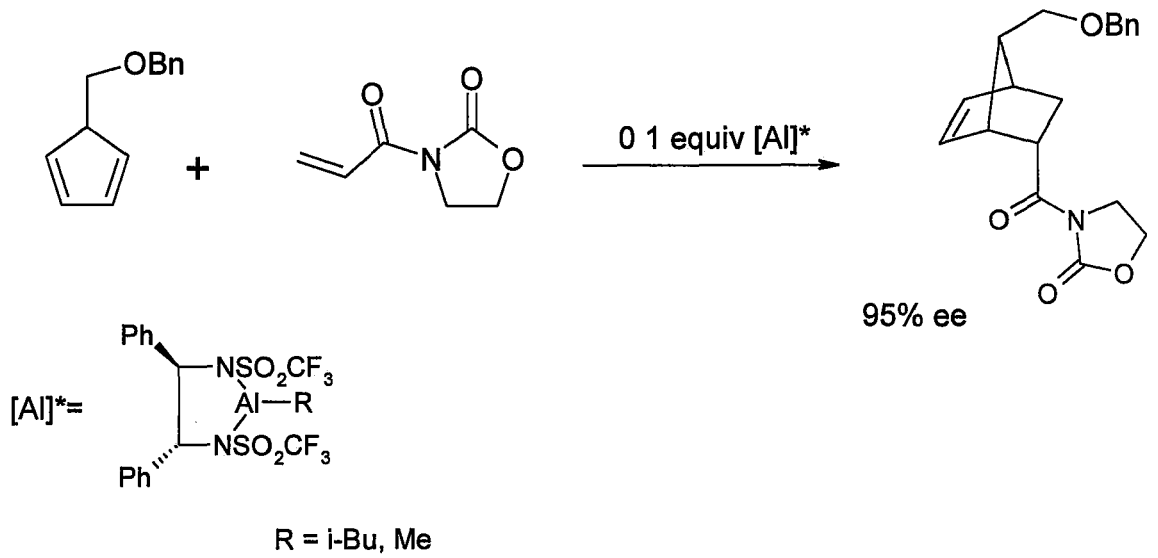


Figure 3. The equation of the cycloaddition between 3-acryloyl-1,3-oxazolidin-2-one and cyclopentadienes, yielding an intermediate useful for production of prostaglandins by Corey et al. [15]

In the area of asymmetric hetero Diels-Alder reactions, H. Yamamoto et al. used a chiral binaphthyl aluminum complex for the efficient condensation of benzaldehyde on a number of dienes (97% ee) as shown in Figure 4a and b.[16-18] Structurally, the catalyst, (cat*) as shown in Figure 4a, contained two silyl functional groups that prevented the strong coordination of the complex with the product. This was the key to its catalytic activity.

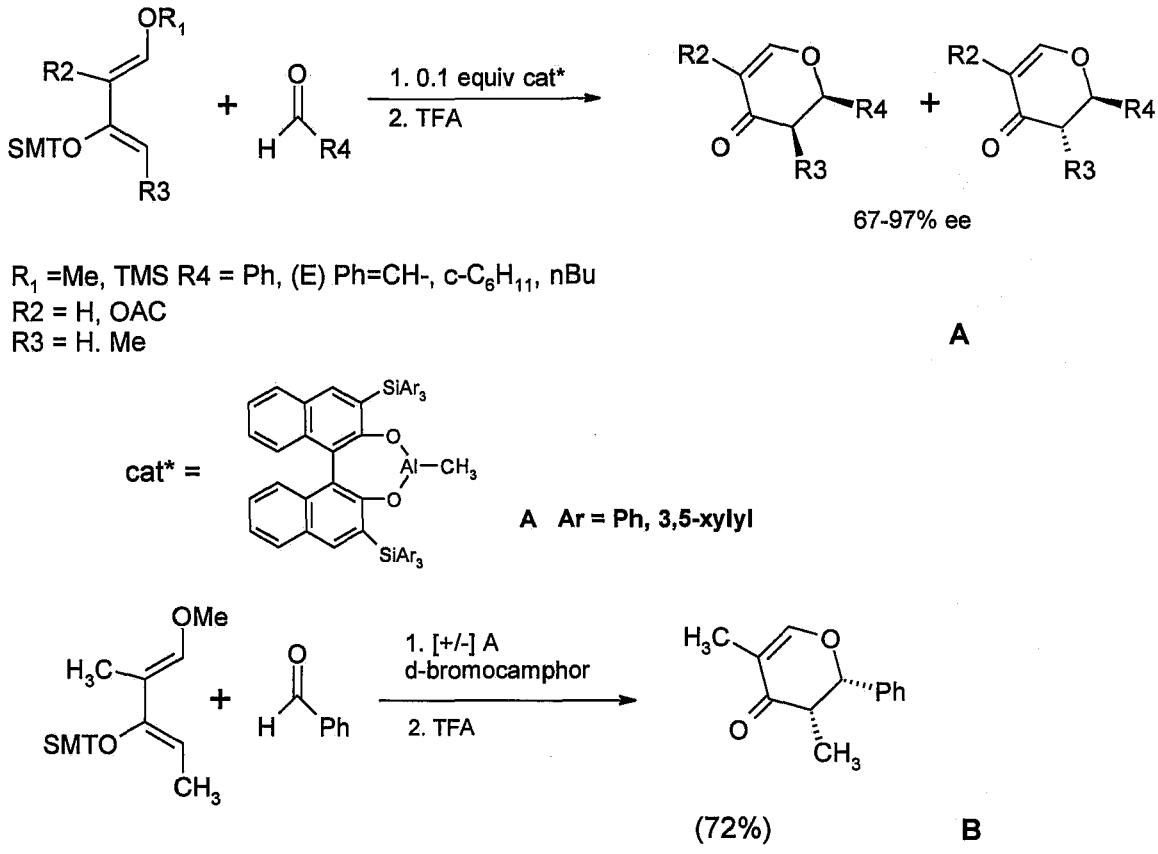


Figure 4. **(A)** The schematic for a general approach to using cat* to produce functionalized dihydropyrones. **(B)** Hetero Diels-Alder reaction is performed in the presence of cat* and (+)-3-bromocamphor, 0.3 mol equiv each, cis-dihydropyrone is isolated with ee up to 80%. Both **A** and **B** were presented by H. Yamamoto et al. [16-18]

Chiral ketones such as 3-bromocamphor can bind selectively one enantiomer of the complex as shown in Figure 4b.[19] Previously, only small ee's in hetero Diels-Alder reaction with menthoxydichloroaluminum as the chiral catalyst had been reported.[20]

A. Chiral Transition-Metal Catalysis

Transition-metals are generally used to catalyze many different reactions because of their ability to change oxidative state. These metals are often very easy to chelate with ligands thus, granting the opportunity to add enantioselectivity to a reaction. In this section, titanium catalysts were separated from other transition-metal catalysts due to the vast quantity of titanium complexes reported in literature.

Chiral alkoxytitanium catalysts were prepared from chiral diols. These catalysts were the first class of complexes successful in the catalysis of Diels-Alder reactions in a one to less than one catalyst to substrate molar ration. In the condensation of cyclopentadiene and acrylamindes or crotonamides, enantiomeric excesses in the range of 90-95% were achieved.[21-23]

Narasaka et al. initially performed cycloaddition with 3-acryl-1,3-oxazolidin-2-ones and cyclopentadiene in the presence of excess titanium complexes.[21] The titanium complex used by Narasaka was prepared from equimolar amounts of a chiral diol and $TiCl_2$ (Oi-Pr)$_2$. The resulting major product was the endo diastereomer with a 92% ee as shown in Figure 5.

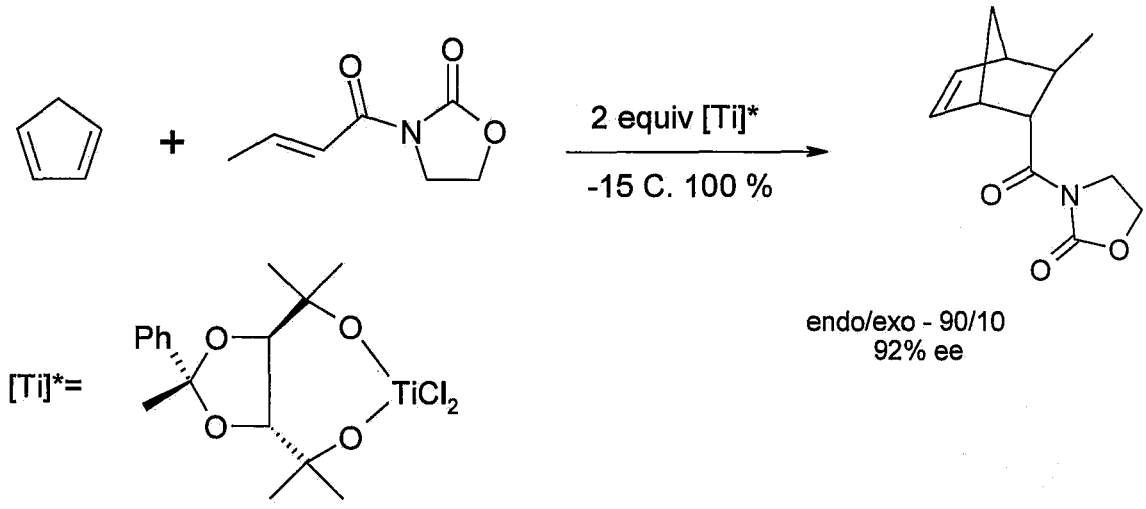


Figure 5. The cycloaddition of 3-acryl-1,3-oxazolidin-2-ones and cyclopentadiene in the presence of titanium complexes by Narasaka et al.[21]

Narasaka et al. initially performed cycloaddition with 3-acryl-1,3-oxazolidin-2-ones and cyclopentadiene in the presence of excess titanium complexes.[21] The titanium complex used by Narasaka was prepared from equimolar amounts of a chiral diol and $TiCl_2$ (Oi-Pr)$_2$. The resulting major product was the endo diastereomer with a 92% ee as shown in Figure 5.

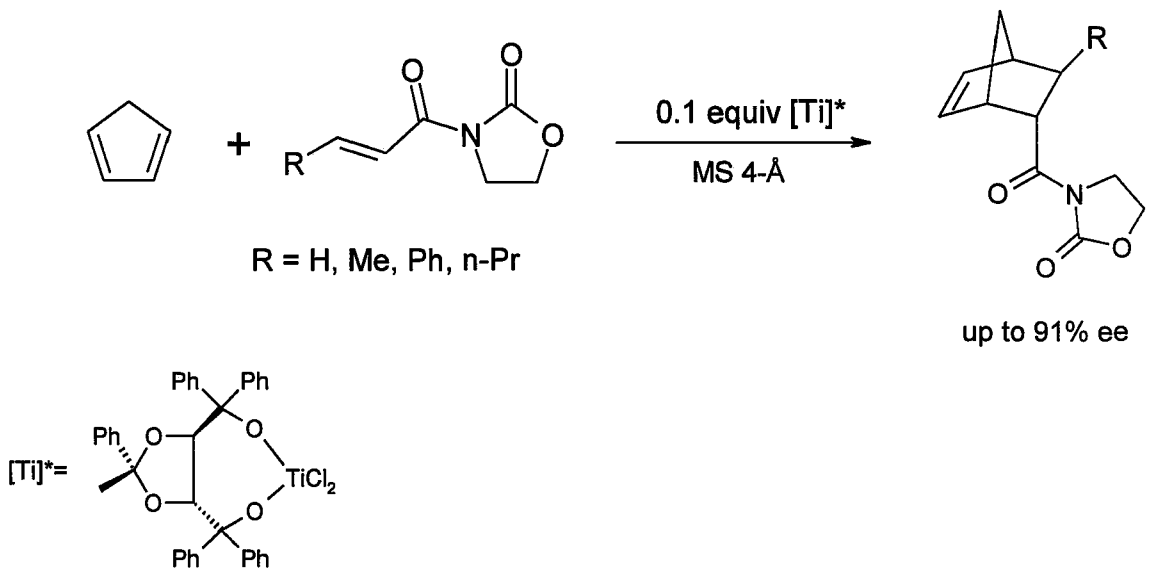


Figure 6. The cycloaddition of 3-acryl-1, 3-oxazolidin-2-ones and cyclopentadiene in the presence of MS 4Å, and a catalytic amount of titanium complexes by Narasaka et al.[22]

Narasaka et al. was also responsible for the use of 4-Å molecular sieves (MS 4Å) in these Diels-Alder reactions, allowing catalytic amounts of dialkoxydichloroitane to be used with optimal enantioselective levels of 90%, very close to that of the stoichiometric reactions, Figure 6.[24-26] This high level of enantioselectivity was explained partially by the removal of water from the reaction mixture.

In the same publication, Narasaka et al. studied the solvent effects on the enantioselectivity of the cycloadducts as shown below in Figure 7. It was found that 1,3,5-trialkylbenzenes greatly enhanced the enantioselectivity of the cycloadducts, as shown in Table 1.

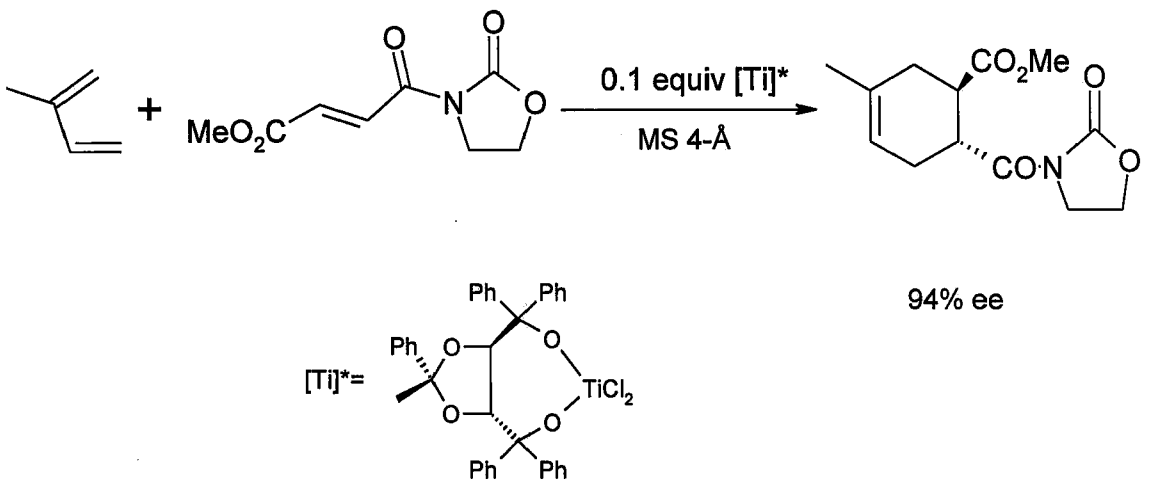


Figure 7. The cycloaddition of 2-Methyl-buta-1,3-diene, and 4-Oxo-4-(2-oxo-oxazolidin-3-yl)-but-2-enoic acid methyl ester in the presence of MS 4Å, and a catalytic amount of titanium complexes. This is the reaction scheme used by Narasaka et al. to test the solvent effects on catalytic Diels-Alder reactions.[21]

Table 1. The results from the solvent study conducted by Narasaka et al. [21]

Solvent	ee (%)
Benzene	41
Toluene	36-68
Mesitylene	96
Methylene chloride	45
Chloroform	52
Tetrachloro-methane	75

Chapius and Jurczak synthesized cycloadducts very similar to those of Narasaka et al. with high ee in the presence of the chiral titanium catalyst, shown in Figure 8 below.[22]

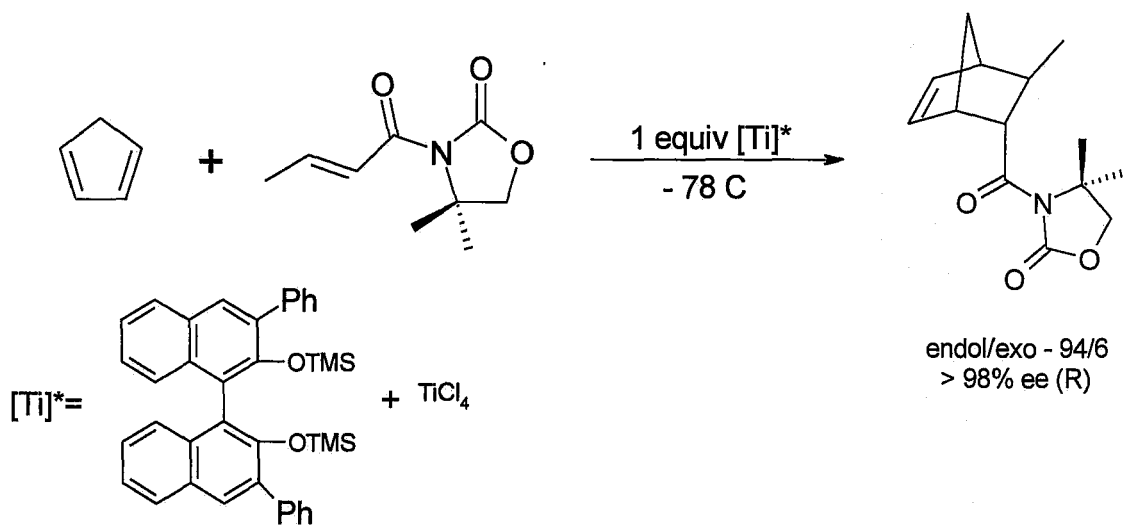


Figure 8. The cycloaddition of 3-But-2-enoyl-4, 4-dimethyl-oxazolidin-2-one, and cyclopentadiene in the presence of titanium complexes by Chapius and Jurczak.

Seebach et al. used an excess of titanium catalyst to condense methyl acrylate and cyclopentadiene (Figure 9).[23]

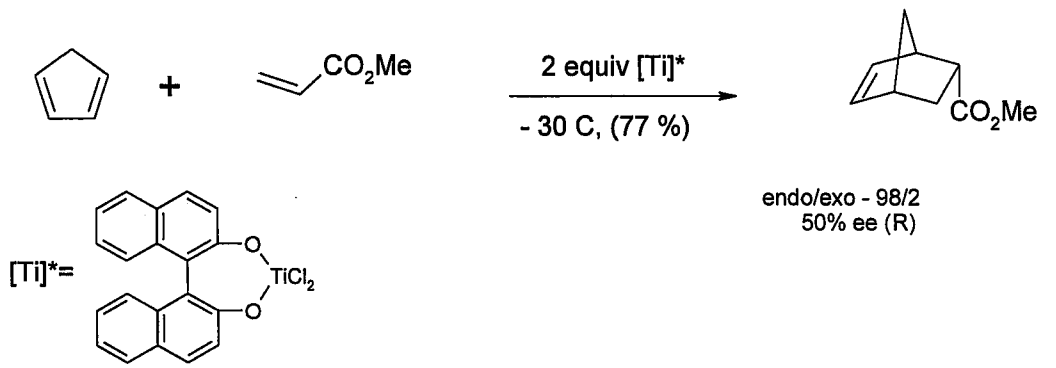


Figure 9. The condensation of methyl acrylate and cyclopentadiene in the presence of titanium catalyst by Seebach et al. [23]

Mikami et al. used this same catalyst to achieve excellent results in a reaction between isoprene and methyl glyoxylate.[23, 27] From this reaction an ene and a hetero Diels-Alder product were formed in high ee, as shown in Figure 10A. The use of this titanium catalyst was extended to other Diels-Alder reactions between 1,3-dienol derivatives and methacrolein, or 1,4-naphtoquinone, and endo selectivity was very high in most cases, as shown in Figure 10B.

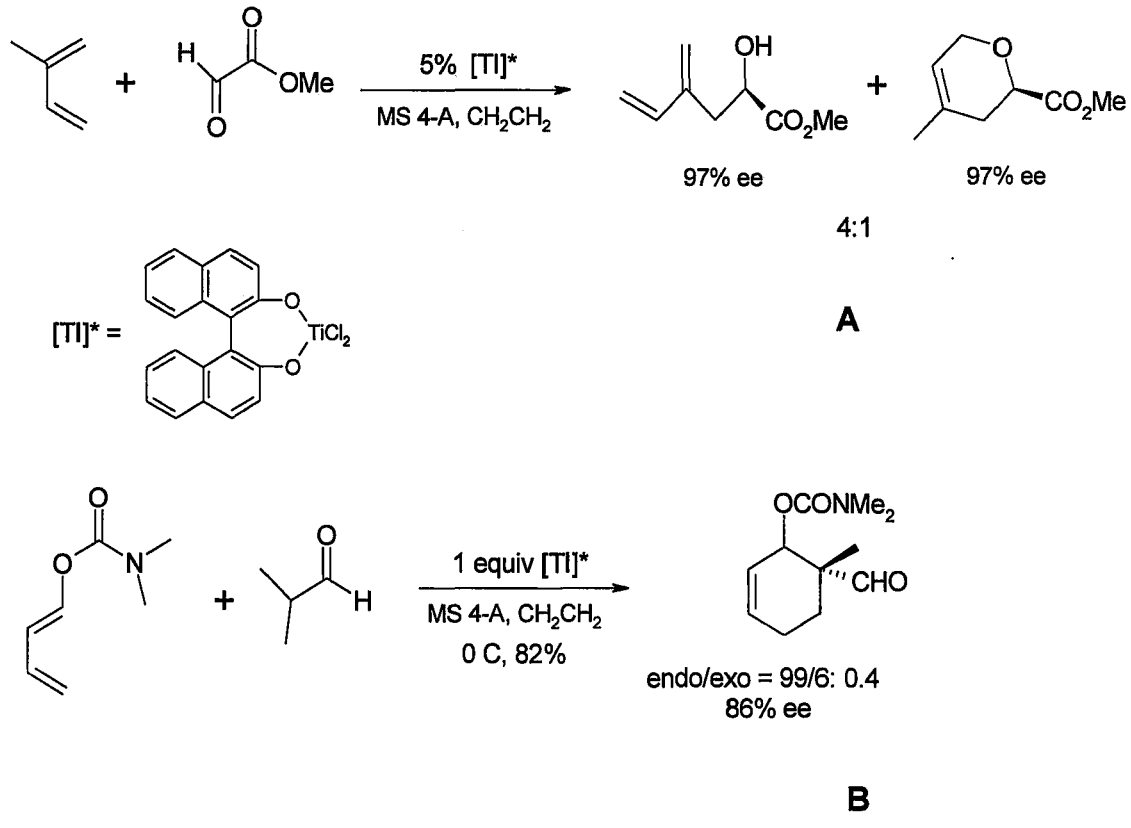


Figure 10. **(A)** A reaction performed by Mikami et al. with isoprene and methyl glyoxylate in the presence of catalytic amounts of a titanium catalyst to produce an ene and a hetero Diels-Alder product.[23] **(B)** An example of Diels-Alder reactions between 1,3-dienol derivatives and methacrolein in the presence of the same titanium catalyst.[27]

Devine and Oh proved that (R,R)-Hydrobenzoin was an effective chiral ligand in the presence of a titanium Lewis acid for the catalytic Diels-Alder reaction with carboxylic ester dienophiles and cyclopentadiene.[28] Devine and Oh achieved yields as high as 91% and ee values as high as 92%. An example of this is shown in Figure 11.

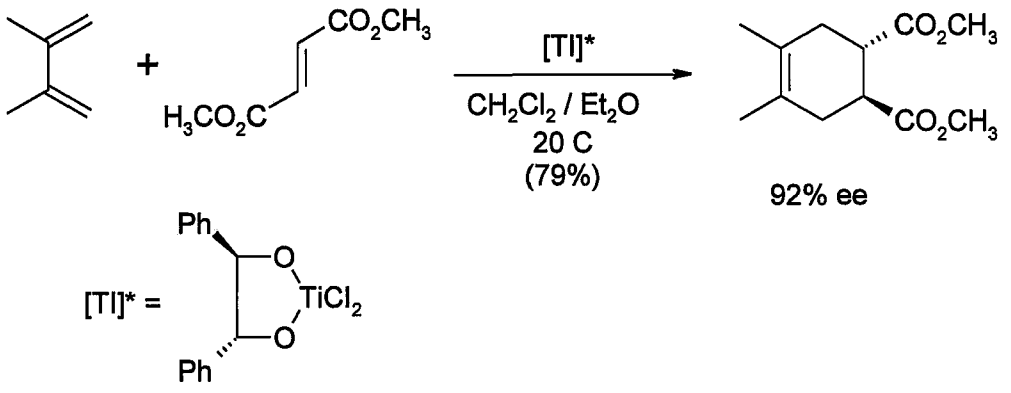


Figure 11. A Diels-Alder reaction with carboxylic ester dienophiles and cyclopentadiene in the presence of a titanium catalyst by Devine and Oh. [28]

In 1993, Yamamoto et al. developed a new helical titanium catalyst from titanium tetraisopropoxide and a chiral ligand derived from optically pure binaphthol.[29] Yields achieved were as high as 77% with ee values from 29-96%. An example of this is shown below in Figure 12.

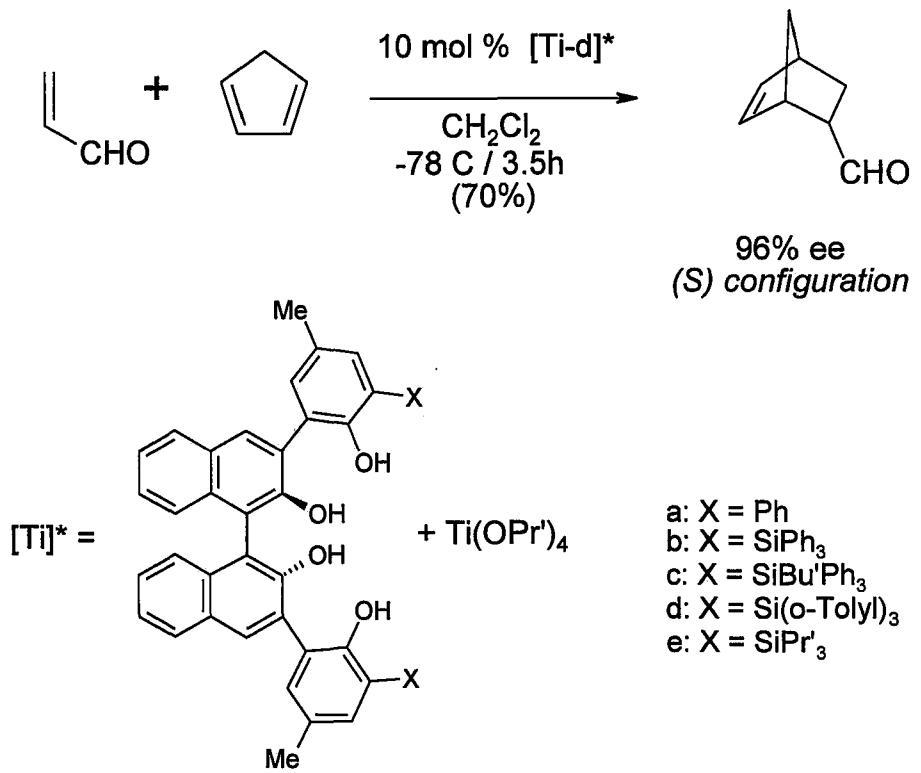


Figure 12. A Diels-Alder reactions with α,β-unsaturated aldehydes and cyclopentadiene in the presence of a helical titanium catalyst by Yamamoto et al. [29]

Bull et al. streamlined the use of binaphthol-titanium complexes for the 4 + 2 cycloaddition of electronically matched 2-pyrones and vinyl ethers to synthesize A-ring precursors to physiologically active 1-hydroxyvitamin D_3 steroids. [30] An example is shown in Figure 13. Bull et al. obtained yields from 86-90% and ee values from 95-98%.

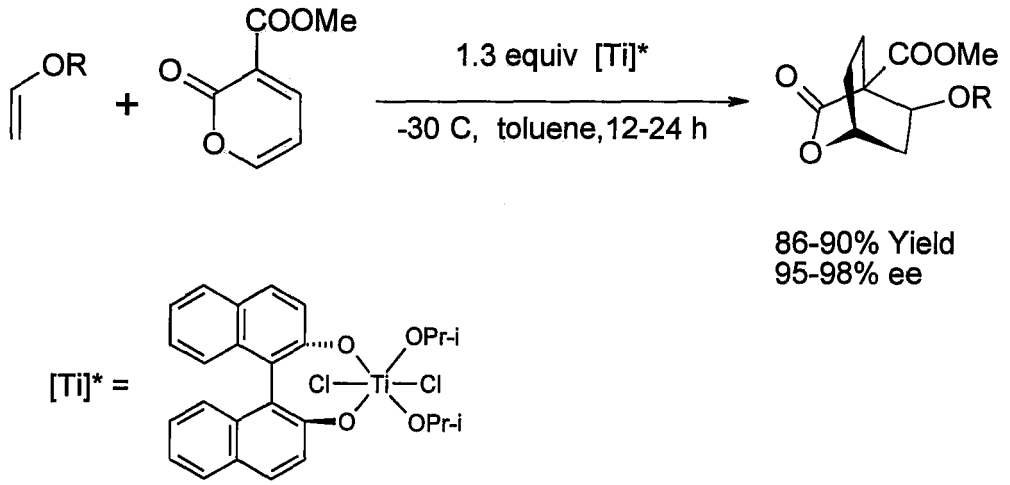


Figure 13. Bull et al. model for synthesizing A-ring precursors to physiologically active 1-hydroxyvitamin D_3 steroids.[30]

In 1997, Matsukawa and Mikami demonstrated the importance of chiral activators in the asymmetric catalysis of Diels-Alder reactions by chiral titanium(IV) complexes.[31] This was achieved by mixing chiral diols such as binaphthol and titanium tetraisopropoxide at a 1:1 ratio in toluene for 20 min. and adding chiral activators such as binaphthol. With the results from this experiment, Matsukawa and Mikami concluded that an asymmetric activation provided enhanced levels of catalyst efficiency and enantioselectivity over that of an enantiomericlly pure catalyst.

In 1999, Manickam and Sundararajan published work on a new tridentate ligand in which they studied a catalytic Diels-Alder reaction with Evans' oxazolidinones as

dienophiles and cyclopentadiene, with high yields of adducts and moderate ee values reported.[32] A structure of this ligand is shown in Figure 14.

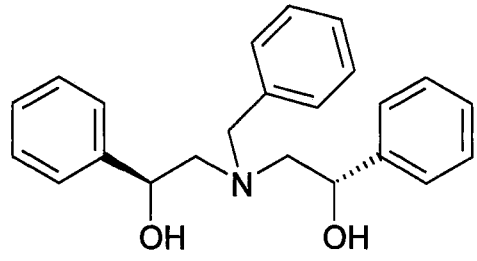


Figure 14. A chiral tetradentate synthesized by Manickam and Subdararajan to be used in the presence of titanium Lewis acids catalytically for Diels-Alder reactions. [32]

More recently, catalytic use of titanium derivatives was investigated by Wang et al., who performed Hetero-Diels-Alder reactions with aldehydes and Danishefsky's diene that yielded enantioselective up to 99% ee and yields of 92%, as shown in Figure 15.[33]

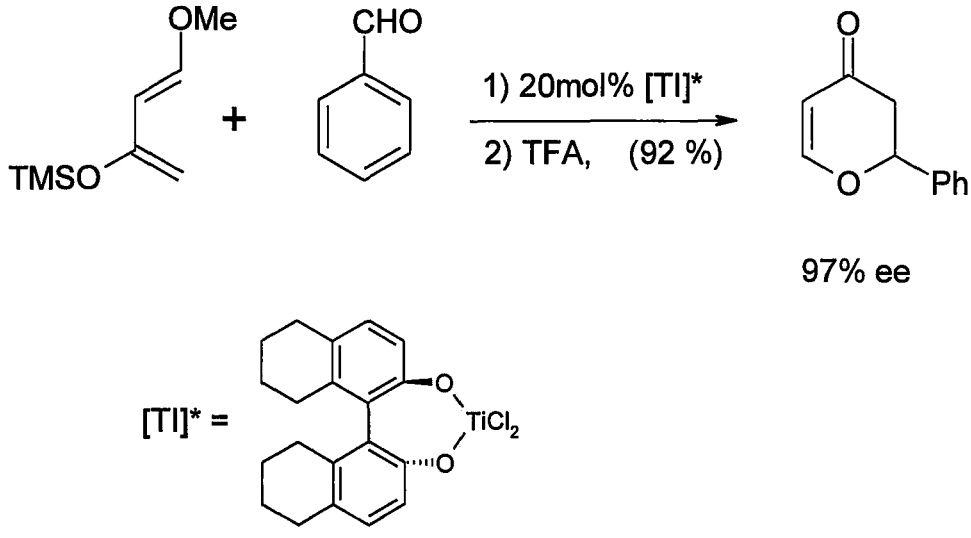


Figure 15. A Hetero-Diels-Alder reaction with aldehydes and Danishefsky's in the presence of a titanium catalyst by Wang et al. [33]

Fan et al. also performed Hetero-Diels-Alder reactions using Brassard diene with aromatic aldehydes in the presence of a titanium(IV) tetradentate Schiff base complex to five δ-lactones in very high ee (up to 99%) under mild conditions. An example is shown in Figure 16.[34]

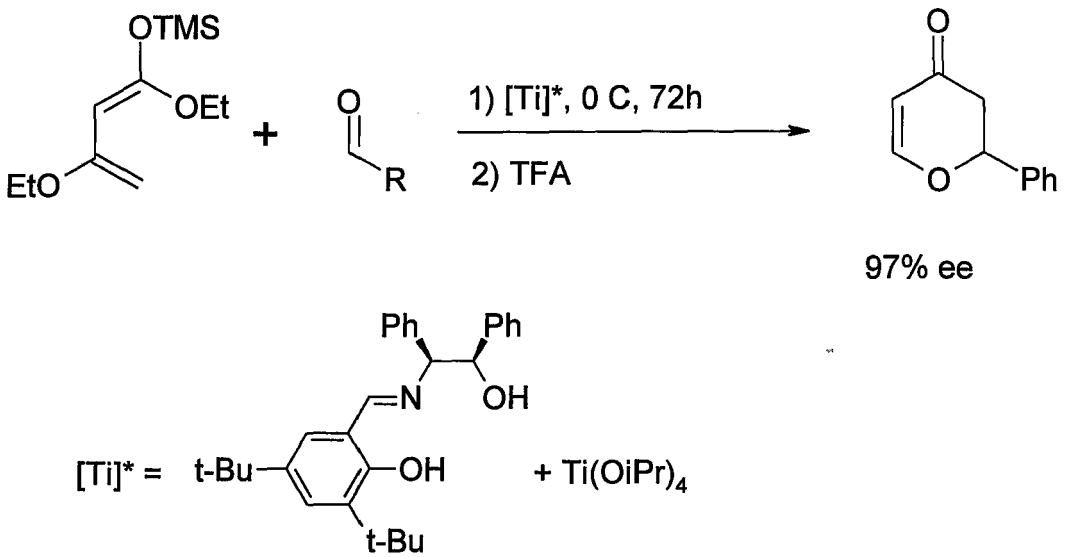


Figure 16. A Hetero-Diels-Alder reaction with Brassard diene and aromatic aldehydes in the presence of a titanium (IV) tridentate Schiff base complex by Fang et al. [34]

Although titanium(IV) is a very special transition metal for Diels-Alder catalysis, it is not the only transition metal capable of initiating Diels-Alder reactions. The catalytic capacity of other transition metals such as copper(II), Co(II) and Fe(II) to name a few, have been well documented.

In the early '90s, chiral bis-ox-azolines coupled with various transition metals were critically being examined as Diels-Alder initiators.[35] Some of the earlier examples were moderate at best.

During this period, many iron complexes displayed high potential for catalyzing Diels-Alder reactions. A few examples are $[W(Me_3P)(NO)(CO_3)_3](FeSbF_4)$, ferricinium hexafluorophosphate,[36] and $[(\eta_5\text{-}Cp)Fe^{+}(CO)P(OMe)_3](THF)(BF_4^{-})$.[37] Honeychuck et al.

published work that contained the crystal structure of an acrolein tungsten complex (catalytically active), which reveals the coordination of carbonyl oxygen to tungsten.[38]

Corey et al. prepared a ferric Lewis acid, L^*FeX_2I, prepared in situ by treatment of anhydrous FeX_2, X = halogen, and ligand L* followed by oxidation of the ferrous complex with iodine. Ferric complex catalyzes the Diels-Alder reaction between cyclopentadiene and bidentate dienophile; the cycloadducts were isolated with 86% ee and 99/1 endo/exo diastereo selectivity (Figure 17).[39]

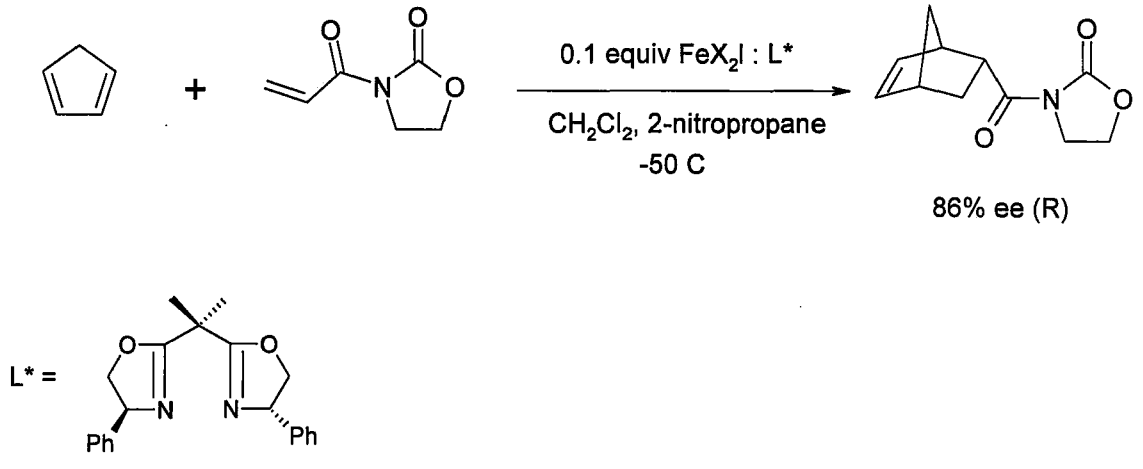


Figure 17. A Hetero-Diels-Alder reactions cyclopentadiene and bidentate dienophile in the presence of a chiral bis-ox-azolines ferric complex by Corey et al. [39]

Faller et al. proved that Ruthenium complexes were capable of catalyzing Diels-Alder reactions. Faller et al. used a $[(\eta_5\text{-Cp})Ru(Ph_3)_2(CH_2CH_2]^+PF_6^-$ to catalyze hetero

Diels-Alder reaction between Danishefsky diene and benzaldehyde, with moderate ee results (Figure 18). [40]

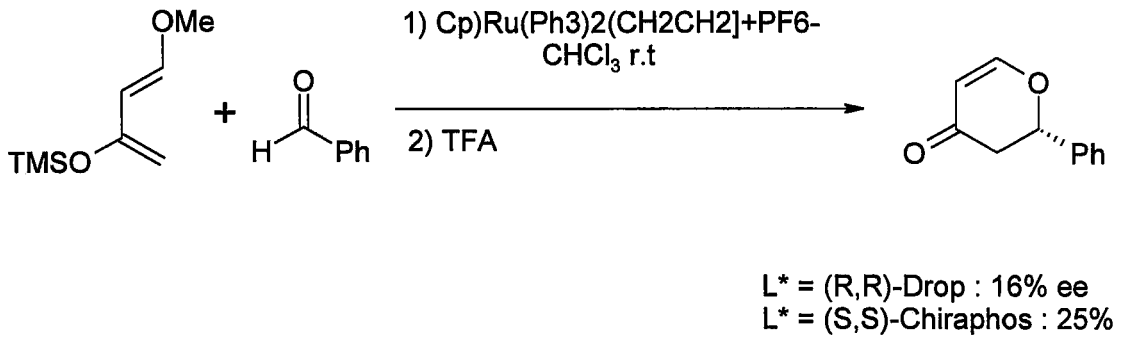


Figure 18. A Hetero Diels-Alder reaction between Danishefsky diene and benzaldehyde in the presence of a ruthenium complex by Faller et al. [40]

Around this same time, Togni et al. reported that fair to good ee's were obtained in the asymmetric catalysis of the Hetero Diels-Alder reaction by oxovanadium(IV) complexes bearing camphor-derived 1,3-diketonato ligands, (Figure19A and 19B).[41] Although under the same conditions, Brassard's diene and cinnamaldehyde furnished the kaiwain lactone with rather low optical yields.

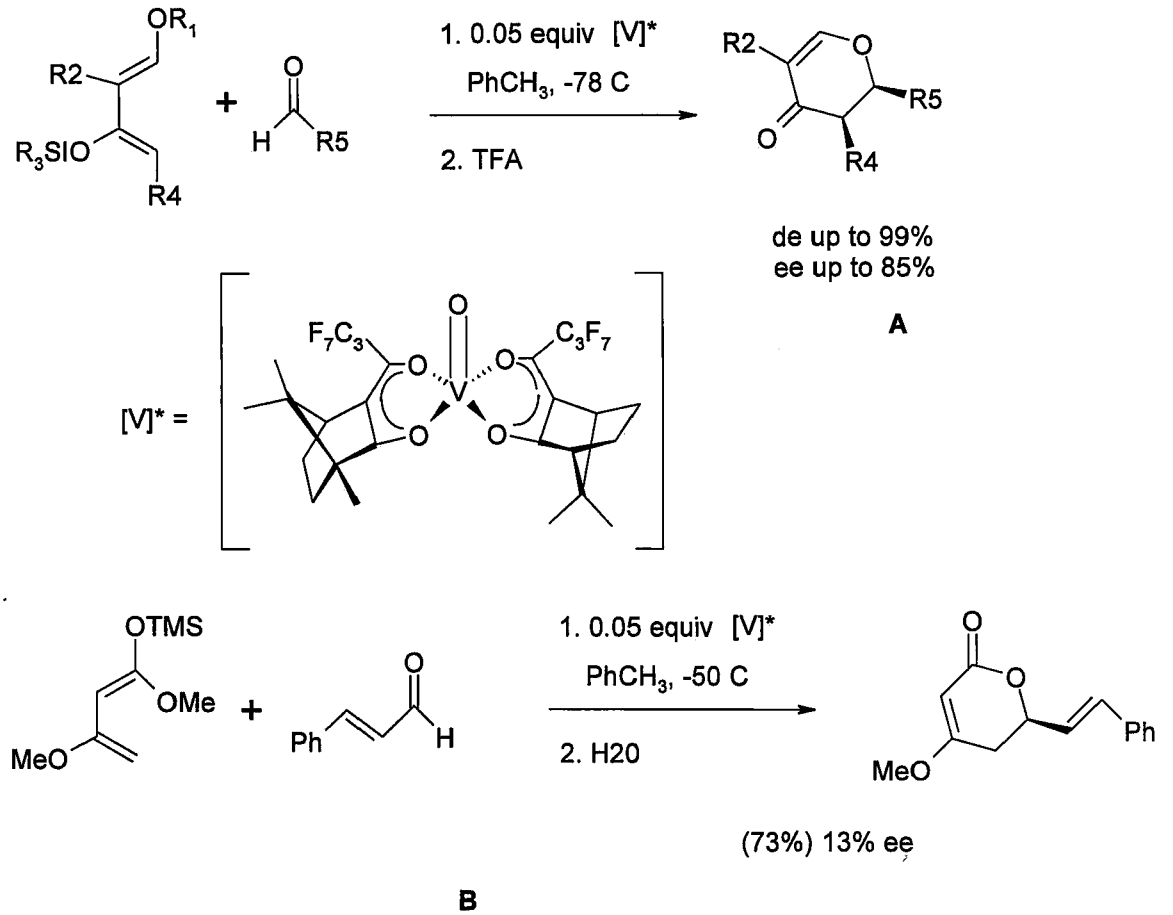


Figure 19. A Hetero Diels-Alder reaction by oxovanadium(IV) complexes bearing camphor-derived 1,3-diketonato ligands by Tongi et al. [41]

It is well known that homo-Diels-Alder reaction ([2 + 2 + 2] cycloaddition) between norbornadiene and an olefin, or monosubstituted acetylene, can be performed with the help of nickel or cobalt catalysts.[42] Early on, this method gave rise to deltacyclane or deltacyclene skeletons with formations of up to six new stereo centers in a single step. Lautens et al. and Brunner et al. asymmetrically modified these catalysts

and reported high enantiomeric excesses in both cases.[43-44] Lautens et al. and Brunner et al. first investigated the effectiveness of the chiral-modified nickel catalyst, which was basically a combination of nickel(II) cyanide and chiral diphosphines,[44a] in the reaction between norbornadiene and acrylonitrile. This catalyst yielded disappointingly low enantioselectivity (Figure 20A). The group finally obtained good results with a cobalt catalyst prepared from Co (acac)$_3$, a chiral diphosphine, and excess of $EtAlCl_2$ (based on cobalt). This method proved to be quite general for various mono-substituted acetylenes, and ee in the range of 55-100% could be obtained (Figure 20B).[44a]

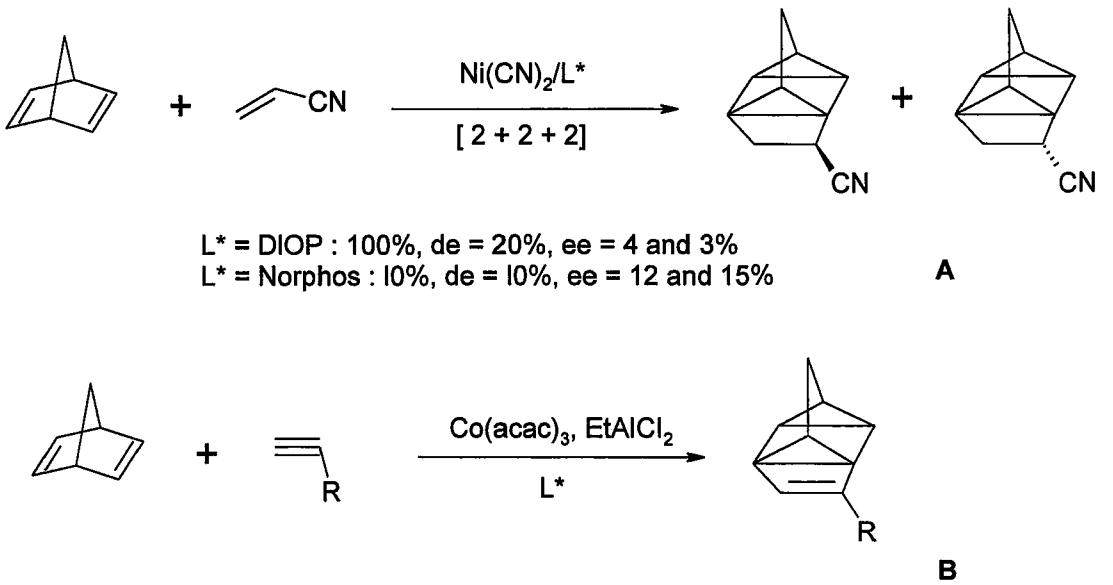


Figure 20. (**A**) A homo-Diels-Alder reaction between norbornadiene and acrylonitrile in the presence of nickel (II) cyanide and a chiral diphosphines. (**B**) A homo-Diels-Alder reaction between norbornadiene and acrylonitrile in the presence of a cobalt catalyst prepared from $Co(acac)_3$, a chiral diphosphine, and excess of $EtAlC1_2$ (based on cobalt). Both performed by Lautens et al. and Brunner et al. [44a]

Corey and Ishihara received high enantioselectivity (20:1) from the cycloaddition of 3-acryloyl-1,3-oxazoline-2-one and cyclopentadiene in the presence of a chiral bis(oxazoline) magnesium complex ion (Figure 21).[45]

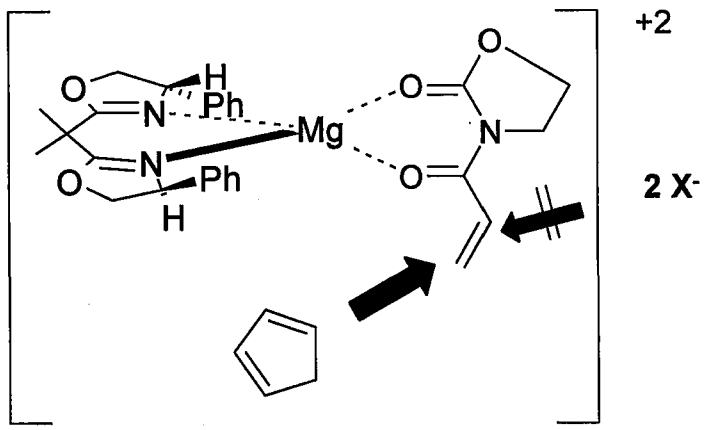


Figure 21. A proposed dipositive complex by Corey and Ishihara for their chiral bis(oxazoline)-magnesium complex.[45]

Takacs et al.[46] took notice of the fact that Zinc(II) salts were very useful Lewis acids that catalyzed transformation in organic synthesis but were poorly represented in the realm of transition-metal complexes for catalysis. As a result, Takacs et al. conducted an extensive study involving the Hetero-Diels-Alder reaction catalyzed by chiral bis(oxazoline) ligands with different lengths of chain connecting the chiral oxazoline subunits, at room temperature, with zinc, magnesium, and copper triflate salts. From the results, these authors concluded that for this particular ligand different metal salts demanded different optimal distances separating the two oxazoline moieties, and that the Zn(II) and Mg(II) complexes had triflate incorporated into their structures. Another result of this research was a successful chiral Zn(II) catalyst for Hetero-Diels-Alder catalysis (Figure 22).

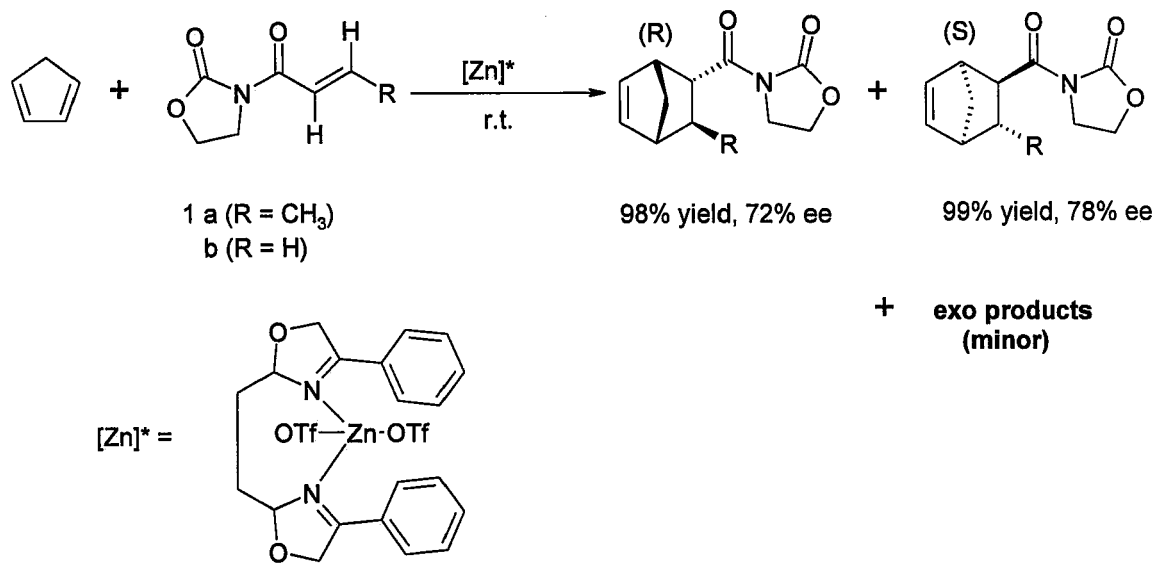


Figure 22. Hetero Diels-Alder reaction with cyclopentadiene and shown dienophile catalyzed by chiral bis(oxazoline)-zinc complex. [46]

Around the same period, Evens et al. catalyzed a Diels-Alder reaction of acryloyl oxazolidinone and 1-acetoxy-3-methylbutadiene to synthesize a precursor for Δ^1-tetrahydrocannabiol, with a cationic bis(oxazoline) Cu(II) complex. This author achieved an ee of 98% (73:27) exo:endo (Figure 23).[47]

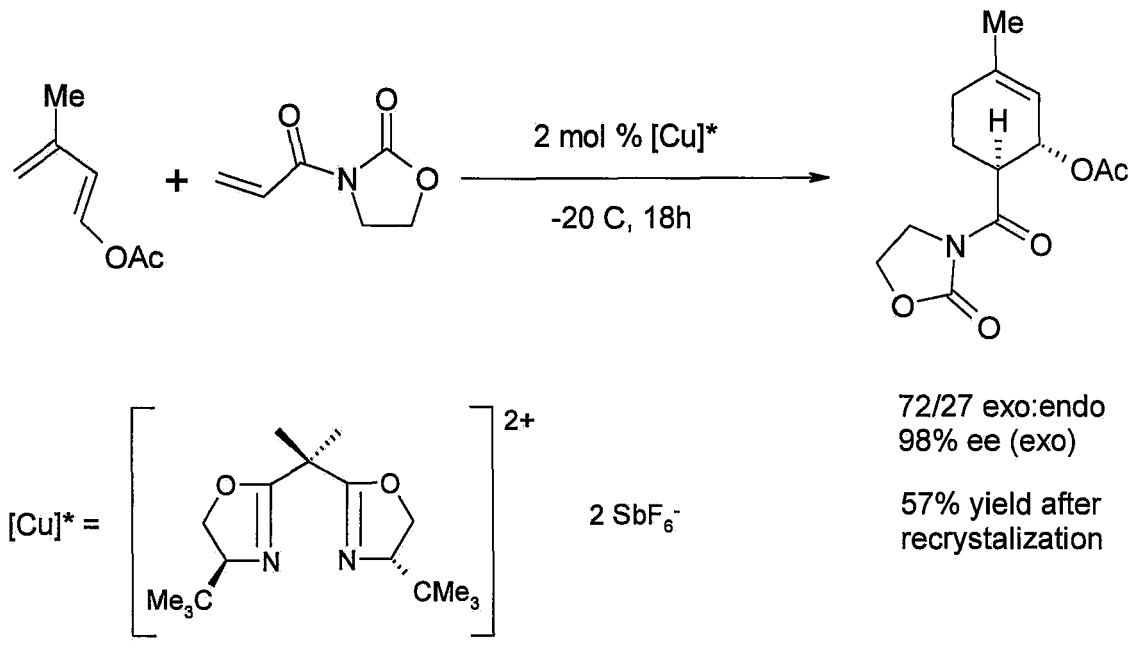


Figure 23. Hetero Diels-Alder reaction for the synthesis of a Δ^1-tetrahydrocannabiol precursor catalyzed by cationic chiral bis(oxazoline)-copper complex by Evans et al. [47]

In 1998, Li et al. and Hu et al. published individual works using the same (salen) cobalt(II) complex. Li et al. reported the catalytic properties of a chiral (salen) cobalt(II) complex on the hetero Diels-Alder reactions of 1-alkyl-3-(tert-butyldimethylsilyl)oxy-1,3-butadienes with ethyl glyoxulate. The authors achieved a 81% yield of 75%, an endo:exo ratio >99:1, and a moderate ee ≥ 52% (Figure 24).[48]

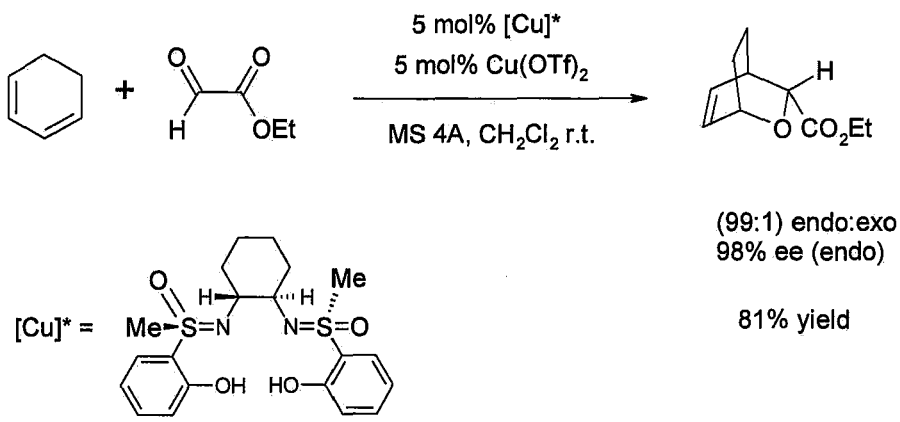


Figure 24. Hetero Diels-Alder reaction of 1-alkyl-3-(tert-butyldimethylsilyl)oxy-1,3-butadienes with ethyl glyoxulate in the presence of a chiral cobalt(II) (salen) catalyst by Li et al.[48]

Hu et al. reported the formal synthesis of 3-Deoxy-D-manno-2-Octulosonic acid via a highly double-stereoselective hetero Diels-Alder reaction, directed by the above mentioned salen catalyst and chiral diene.[49] The reaction is presented in Figure 25, and the results are in Table 2.

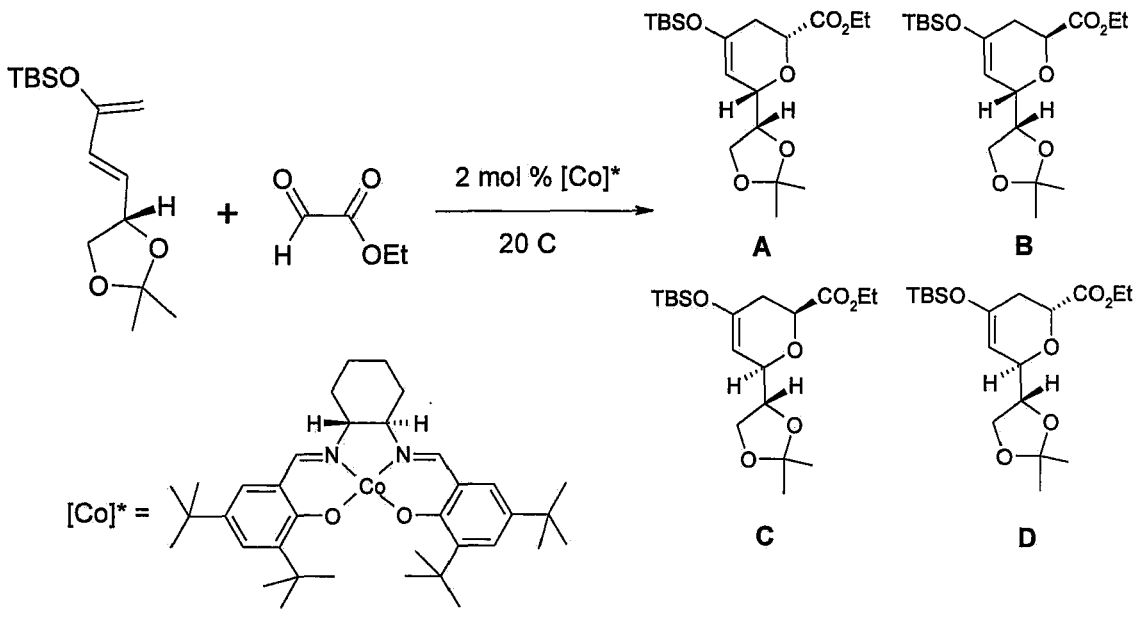


Figure 25. A highly double-stereoselective hetero Diels-Alder reaction directed by the presence of a chiral cobalt(II) (salen) catalyst by Hu et al.[49]

Table 2. A cross section from Hu et al publication, the results for the equation in Figure 25.[49]

Entry	Catalyst	Temp (°C)	Yield (%)	A:B:C:D	*Endo/exo*	*si/ri*
8	**11**	20	85	80:5:13:2	93/7	85/15

Chapman et al. successfully synthesized a series of optically active cobalt(III) salen-1,3-butadien-2-yl complexes.[50] These cobalt(III) complexes (Figure 26) were evaluated in the hetero Diels-Alder reactions to synthesize dimethyl fumarate cycloadducts with ee values from 12-98% and yields from 55-91%.

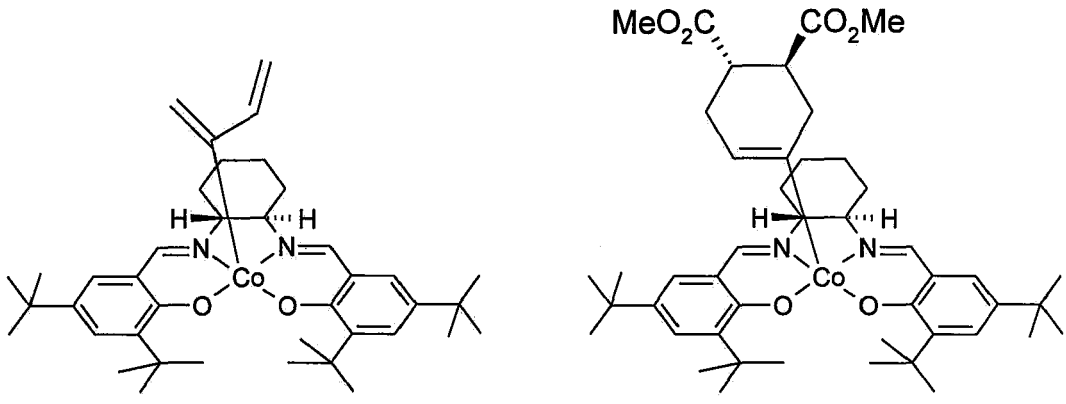


Figure 26. The structure of two optically active cobalt(III) (salen) catalysts by Chapman et al.[50]

Jacobsen et al.[51] studied the catalytic effects of chiral (salen) chromium(III) complex with two different steric groups on a hetero Diels-Alder reaction between Danishefsky's diene and various aldehydes. The authors received high ee values, 93% for A, and 85% for B, with both sterically modified species of chromium(III) catalyst (Figure 27).

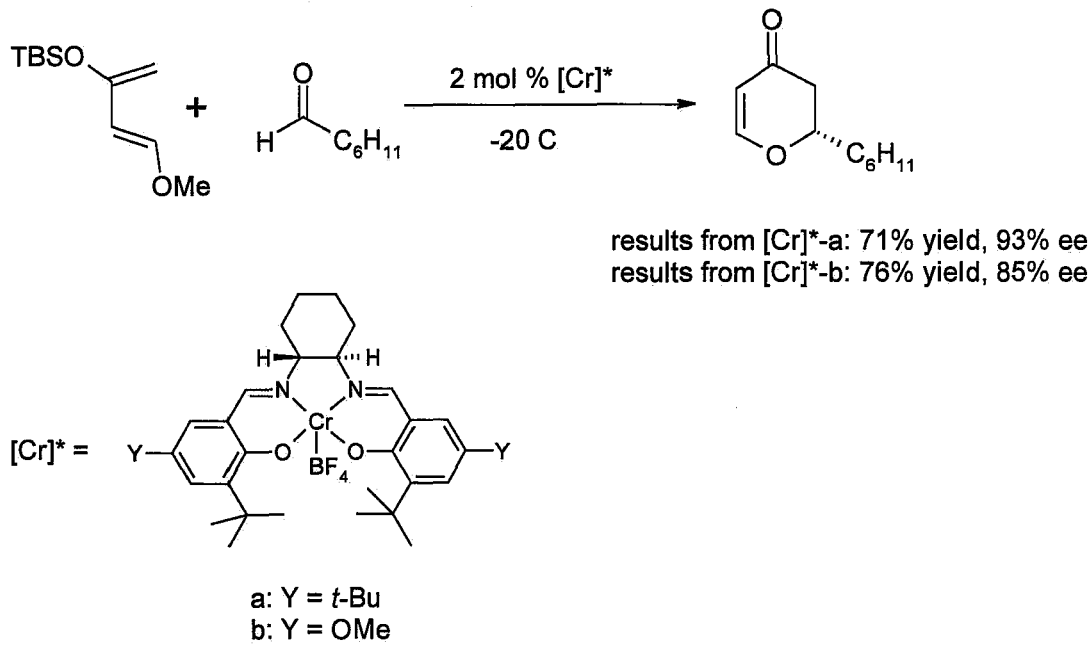


Figure 27. A hetero Diels-Alder reaction between Danishefsky's diene and alkyl aldehyde in the presence of two different chiral (salen) chromium(III) complexes by Jacobsen et al. [51]

Following this work, Jacobsen and Joly closely focused on the diastereoselectivity of the above chromium(III) catalyst and similar catalyst. Jacobsen and Joly developed a methodology that allowed any four of the possible stereoisomers to be achieved in high yields and high ee.[52]

Huang et al. was also successful at performing a hetero Diels-Alder reaction between benzyl buta-1,3-dienyl-carbamic acid methyl ester and 2-Methyl-propenal in the presence of a chromium(III) salen complex with a high enantiomeric excess of 93%, and yield of 99% (Figure 28).[53]

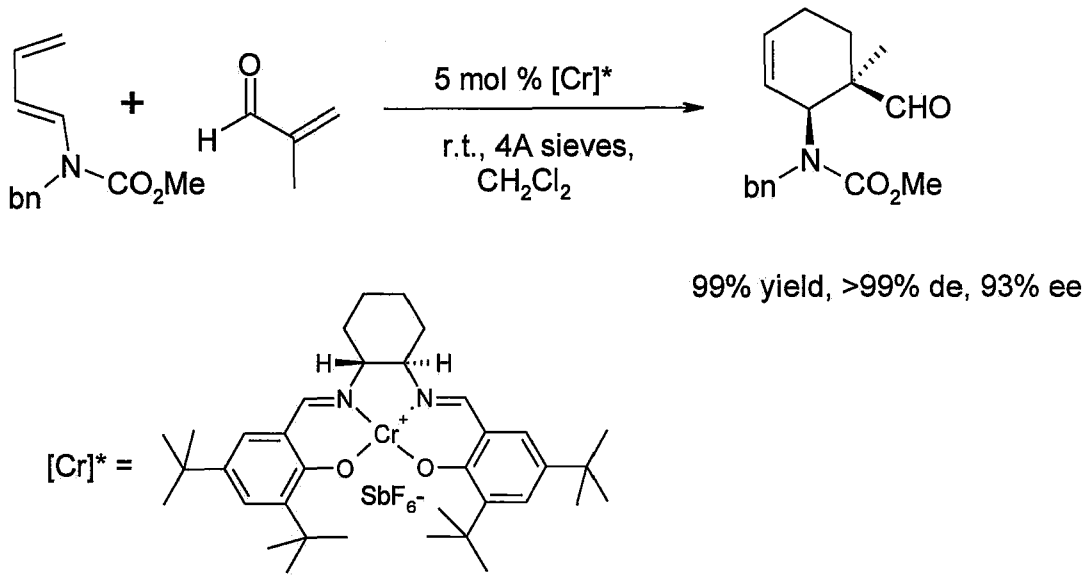


Figure 28. A hetero-Diels-Alder reaction between benzyl-buta-1,3-dienyl-carbamic acid methyl ester and 2-methyl-propenal in the presence of a chromium(III) salen complex by Huang et al. [53]

As a follow-up to the great success Huang et al. received with their asymmetrical chromium(III) salen catalyst, they investigated similar cobalt(III) catalysts and also received high enantiomeric excess (95%, Figure 29).[54]

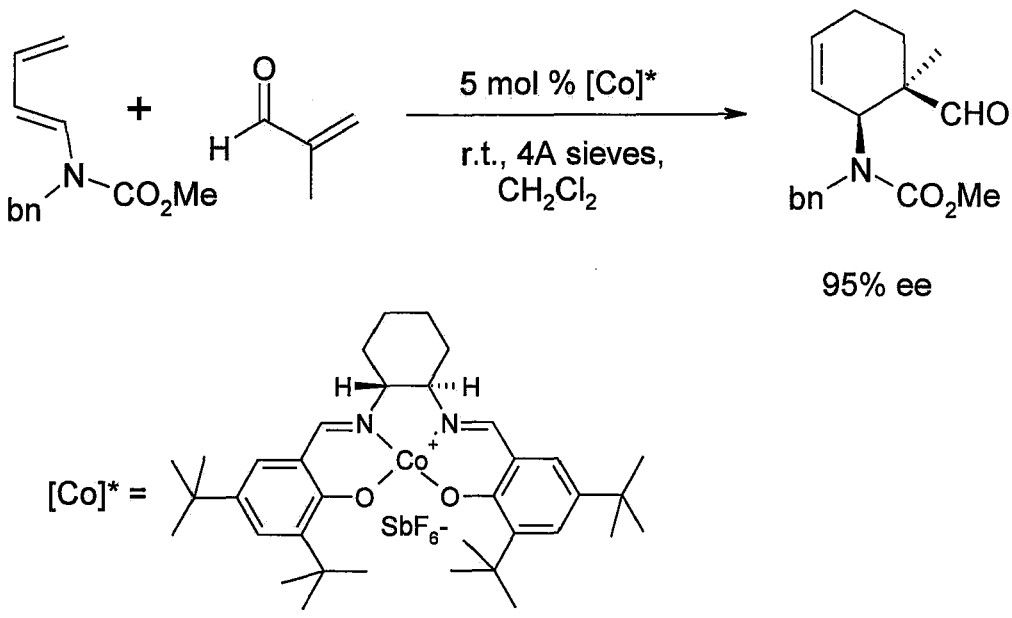


Figure 29. A hetero-Diels-Alder reaction between benzyl-buta-1,3-dienyl-carbamic acid methyl ester and 2-methyl-propenal in the presence of a cobalt(III) salen complex by Huang et al.[54]

Huang et al. studied the interaction of the carbonyl group of the aldehyde and the active site of the cobalt(III) catalyst via X-ray crystal structure to gain critical insight on the activation of the cycloaddition. These authors noticed the congestion of the *tert*-butyl steric groups and hypothesized that this congestion might force the two aromatic rings out of the near parallel arrangement, and thereby accentuate the suiTable helical chirality in the scaffold. With that in mind, they considered an alternative to the *tert*-butyl steric groups. They replaced these groups with o-silyl groups. It was thought that the longer C-Si bond would put the two bay-region substituents, *t*-butyl steric groups, well within van

der Waals radii of one another. Their hypothesis proved right, giving a higher ee value (98%) for the o-silyl modified cobalt(III) salen catalyst, Figure 30.[54]

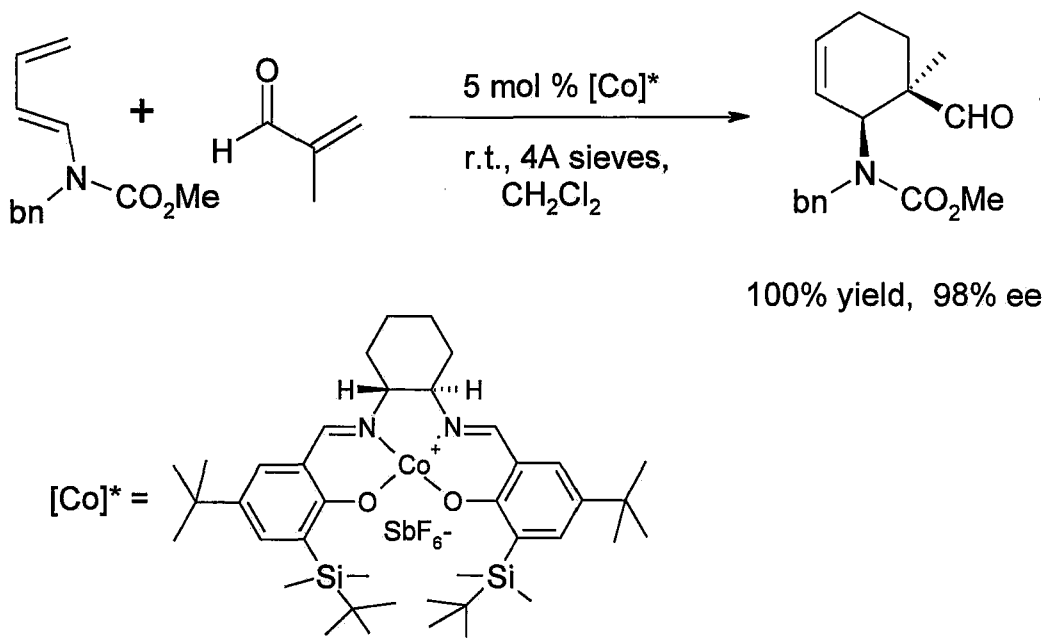


Figure 30. A hetero Diels-Alder reaction between benzyl-buta-1,3-dienyl-carbamic acid methyl ester and 2-methyl-propenal in the presence of a o-silyl modified cobalt(III) salen complex by Huang et al.[54]

Bolm and Simić published work on a hetero Diels-Alder reaction on cyclohexadiene in the presence of a bis(sulfoximine) ligand and copper(II) trifate.[55] They achieved ee values from 92-98% and yields from 62-96% (Figure 31).

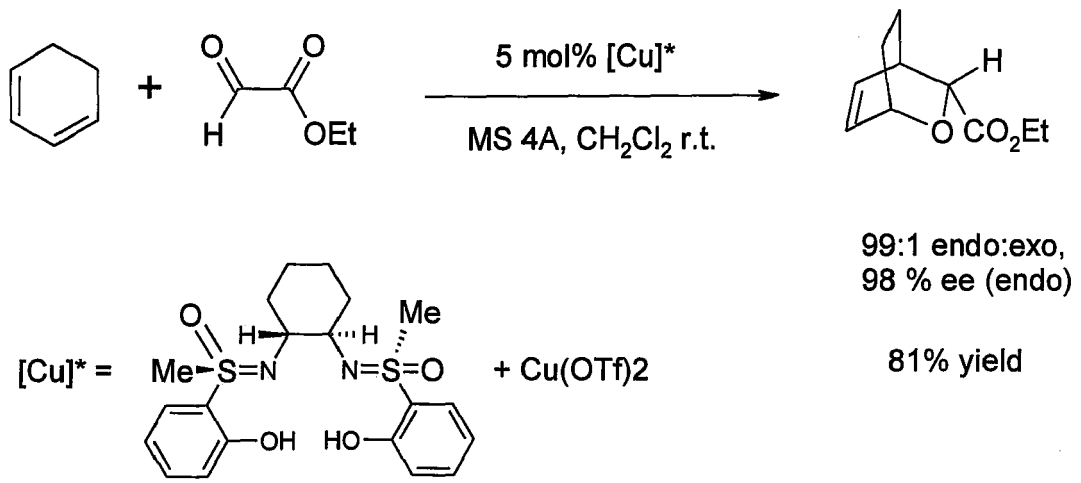


Figure 31. A hetero Diels-Alder reaction with cyclohexadiene and 3-deoxy-D-manno-2-octulosonic acid in the presence of a bis(sulfoximine) ligand and copper(II) trifate by Bolm and Simić. [55]

A homo chiral bis-imine chiral Cu(II) complex synthesized by De Coster et al. yielded moderate ee values (63%) in the cycloaddition of cyclopentadiene and 3-But-2-enoyl-oxazolidin-2-one (Figure 32).[56] The Schiff base ligand used in the catalyst is bidentate.

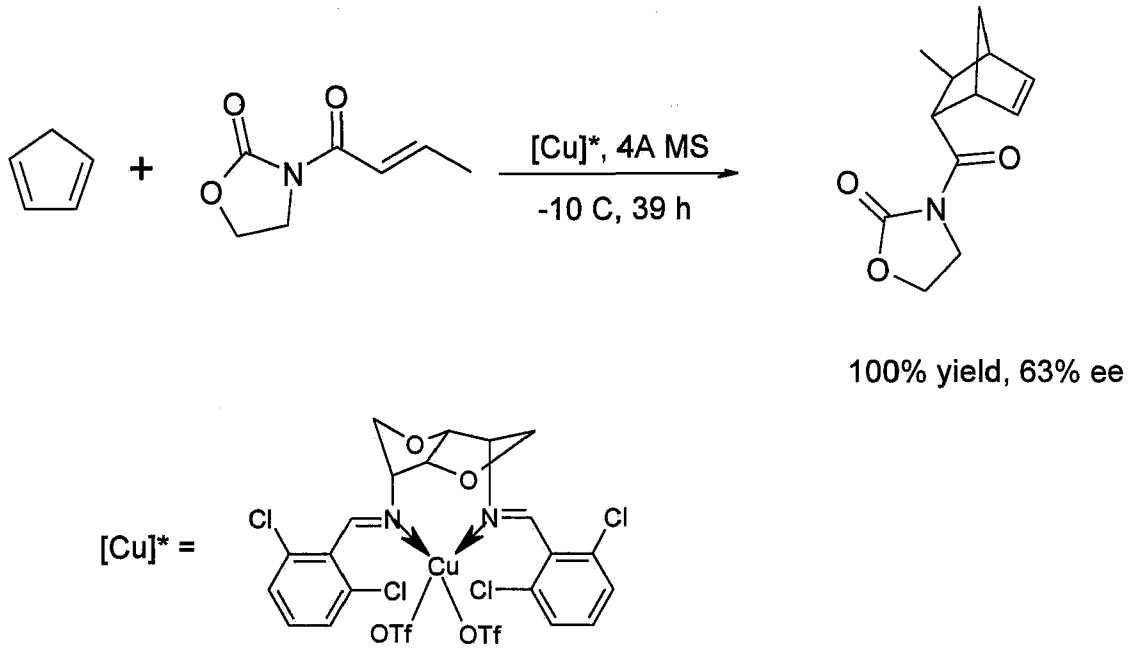


Figure 32. A cycloaddition of cyclopentadiene and 3-But-2-enoyl-oxazolidin-2-one in the presence of a homo chiral bis-imine copper(II) catalyst by De Coster et al. [56]

Owens et al.[57] designed a novel class of ligands based on the sufonyl imine functionality for the copper catalyzed Diels-Alder reaction. The best results were achieved by using the sulfinylimidine ligands in coordination to $Cu(SbF_6)_2$ with ee (98%, Figure 33).

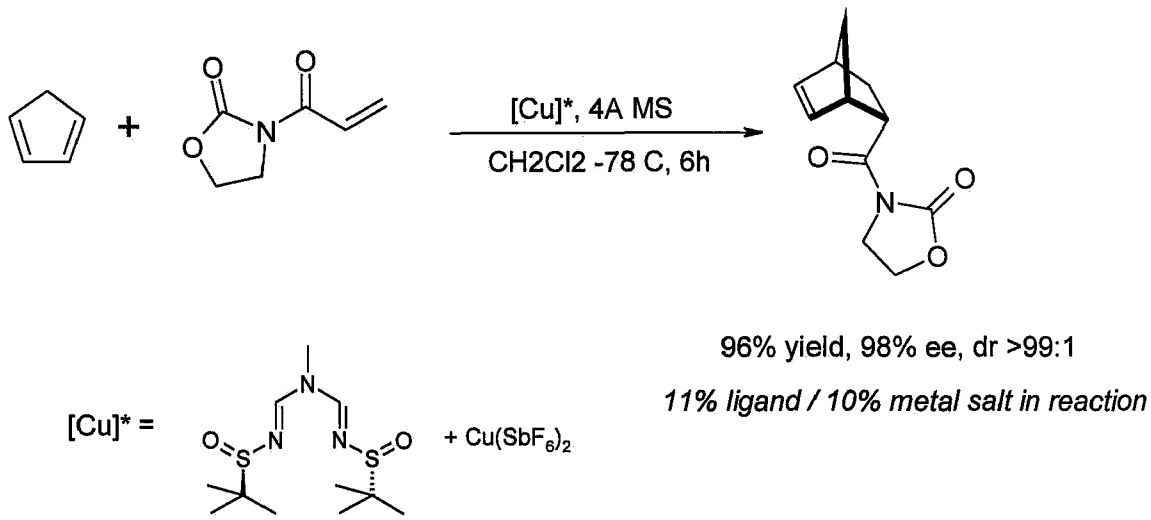


Figure 33. A cycloaddition of cyclopentadiene and 3-prop-2-enoyl-oxazolidin-2-one in the presence of sulfinylimidine ligands in coordination to $Cu(SbF_6)_2$ by Owens et al. [57]

Hiroi and Watanabe received high enantiomericselectivity (92%) from a palladium-catalyzed asymmetric Diels-Alder reaction with a chiral phosphino-oxazoline ligand, Figure 34.[58]

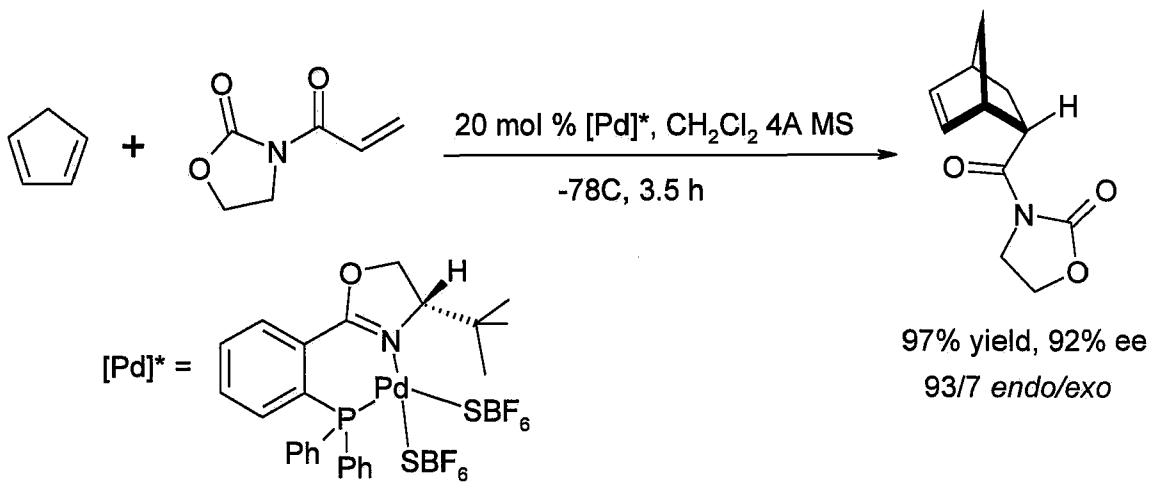


Figure 34. A cycloaddition of cyclopentadiene and 3-prop-2-enoyl-oxazolidin-2-one in the presence of a chiral phosphino-oxazoline Pd(II) catalyst by Hiroi and Watanabe. [58]

More recently, Yamamoto and Yamamoto[59] were successful in obtaining high ee and de values in a (S)-SEGPHOS copper(II) catalyzed nitroso Diels-Alder reaction between 2-nitropyridines and cyclohexadienes (Figure 35).

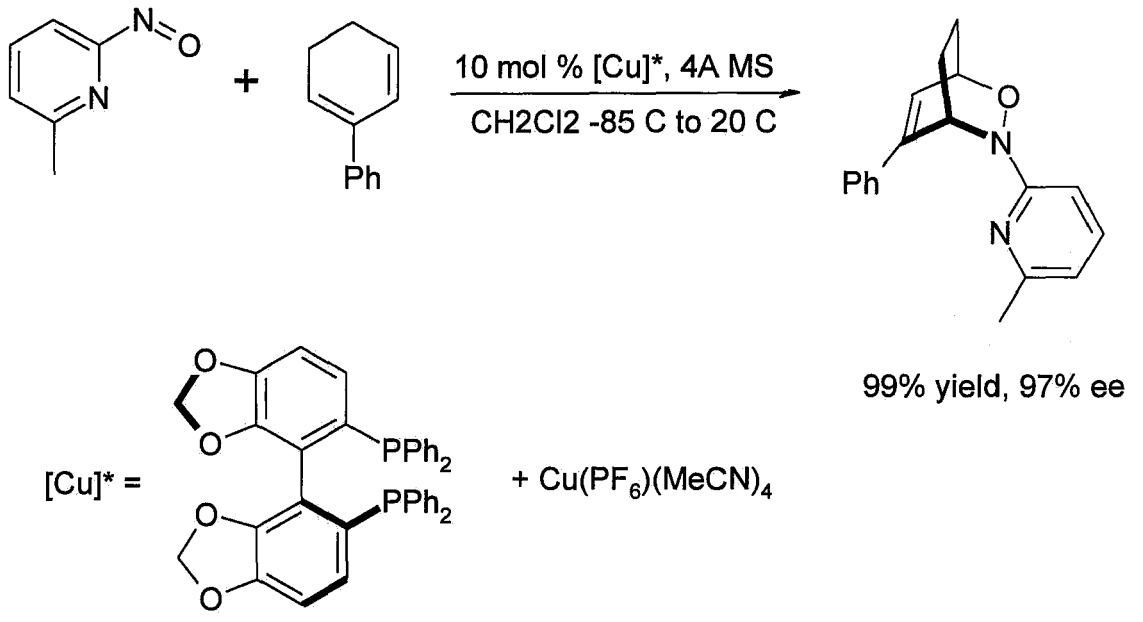


Figure 35. A cycloaddition of Cyclohexa-1,5-dienyl-benzene and 2-Methyl-6-nitroso-pyridine in the presence of a chiral copper(II) catalyst by Yamamoto and Yamamoto.[59]

CHAPTER III

RESULTS AND DISCUSSION

The class of Schiff bases, commonly known as salen, is tetradentate and its members have proven to be excellent ligands. Chirality can even be introduced into the bis-Schiff bases via chiral diamines and salicylaldehydes. Different metals, e.g., transition metals, easily complex with salen type ligands to form metal Schiff base complexes with exceptional yields. Hence, the Schiff base scaffold was used for the following reasons: (1) Schiff base ligands are relatively stable under most conditions and can be stored; (2) Schiff base ligands can be efficiently synthesized with various chiral diamines or salicylaldehydes; and (3) Schiff base ligands are also cost effective and simple to synthesize. Various substituted Schiff base ligands were synthesized to develop a highly enantioselective catalyst for hetero Diels-Alder reactions.

A. Salicylaldehydes

The preparation of salicylaldehydes is a very important portion of salen ligand synthesis. The synthesis of salicylaldehydes begins with substituted phenols, which are usually commercially available or easily synthesized via Friedel-Crafts alkylation.

The phenols are then formylated to generate salycilaldehydes in exceptional yields. Generally there are four methods favored for the synthesis of salicylaldehydes:

(1) Rieman-Tiemer,[60] (2) Duff,[61] (3) Tin(IV) tetrachloride in the presence of triethylamine for phenoxide,[62] and (4) a catalytic method developed by Sidney Lang.[2] Logically, the latter method would be the best choice, given that it exhibits exceptionally high yields (94-98%) with only a catalytic amount of titanium(IV) tetrachloride, in contrast to the Rieman-Tiemer method, which only yields 40-60% with an excess of tin(IV) tetrachloride and the Duff method where para-substitution is more favorable. Although this group's method of formylation was the most efficient, we decided to use the Rieman-Tiemer method due to the excess of tin(IV) tetrachloride available upon initiating these reactions.

3,5-Di-*tert*-pentylsalicylaldehyde **(2)** was prepared by a procedure described by Lang et al. 2,4-di-*tert*-pentylphenol **(1)** was reacted with 2,6-lutidine (0.4 equiv.), tin(IV) tetrachloride (0.1 equiv.), and paraformaldehyde (3.3 equiv.) in dry toluene to give 3,5-di-*tert*-pentylsalicylaldehyde **(2)** (40-60%, scheme 1).

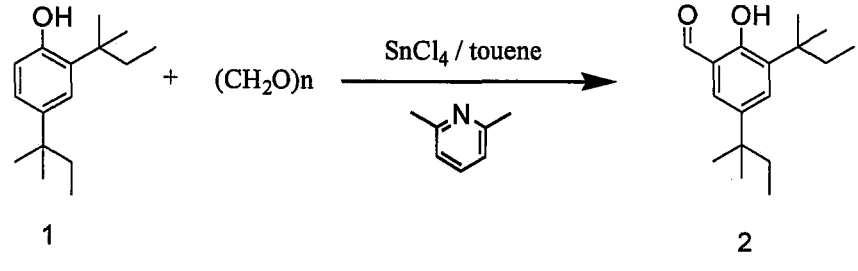


Figure 36: Reaction Scheme for the synthesis of 3,5-di-*t*-pentyl-2-hydroxybenzaldehyde (2).

B. Chiral and Achiral Diamines

1,3-Diamino-propan-2-ol (**3**), benzene-1,2-diamine (**4**), ethylene-1,2-diamine (**5**), (S,S)-1,2-diamino-1,2-diphenylethane (**6**), and (R,R)-1,2-diaminocyclohexane (**7**) were chosen as the backbone for the Schiff base ligands. 1,3-diamino-propan-2-ol, benzene-1,2-diamine, and (S,S)-1,2-diamino-1,2-diphenylethane were obtained commercially.

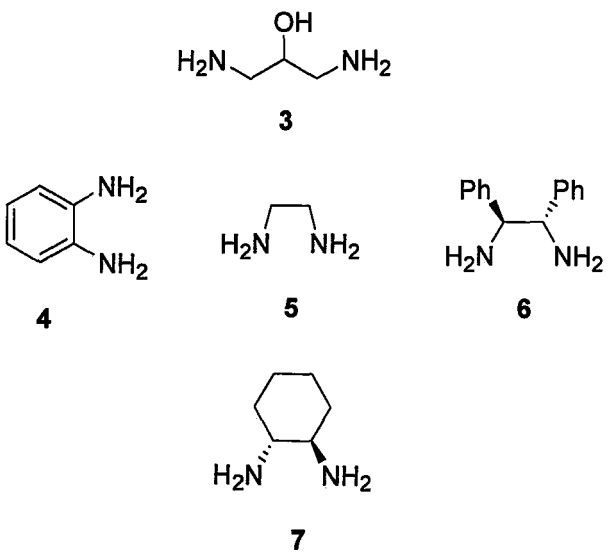
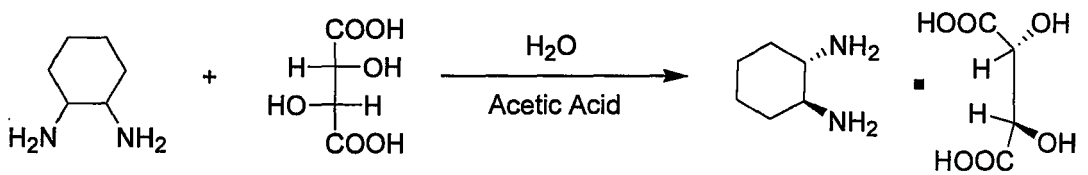


Figure 37. Diamines used to synthesize Schiff base ligands.

Optically pure 1,2-diaminocyclohexane was resolved from the racemic mixture, obtained commercially, using a method decribed by Jaeger et al.[63] Cis/trans-1,2-diaminocyclohexane (**8**) was treated with L-(+)-tartic acid (**9**) with yielded (R,R)-1,2-

diaminocyclohexane tartrate **(10)** in a 96% yield, reaction scheme 2. The diaminocyclohexane tartrate was then recrystallized from water to yield 60-70% optically pure (R,R)-1,2-diaminocyclohexane tartrate. The optical rotation measured for product (R,R)-1,2-diaminocyclohexane tartrate **(10)** ($[\alpha]_D^{25}$+12.5 (c=4, H_2O) indicated that it was >99% optically pure. (R,R)-1,2-diaminocyclohexane tartrate **(9)** was directly condensed with salicylaldehyde to produce Schiff base ligands without any further purification.



8 **9** **10**

Figure 38: Reaction Scheme for the resolution of 1,2-diaminocyclohexane (8).

C. Schiff Base Ligands

The Schiff base ligands were synthesized by the condensation of diamino derivatives **(3-7)** and 3,5-di-*tert*-pentylsalicylaldehyde **(2)**. These reactions produced high yields in most cases, and the resultant ligands (**12-15**, Figure 39 and 40) were purified by recrystallization. Due to the degradation of Schiff base ligands on silica and alumina gel columns, the use of such methods was avoided.

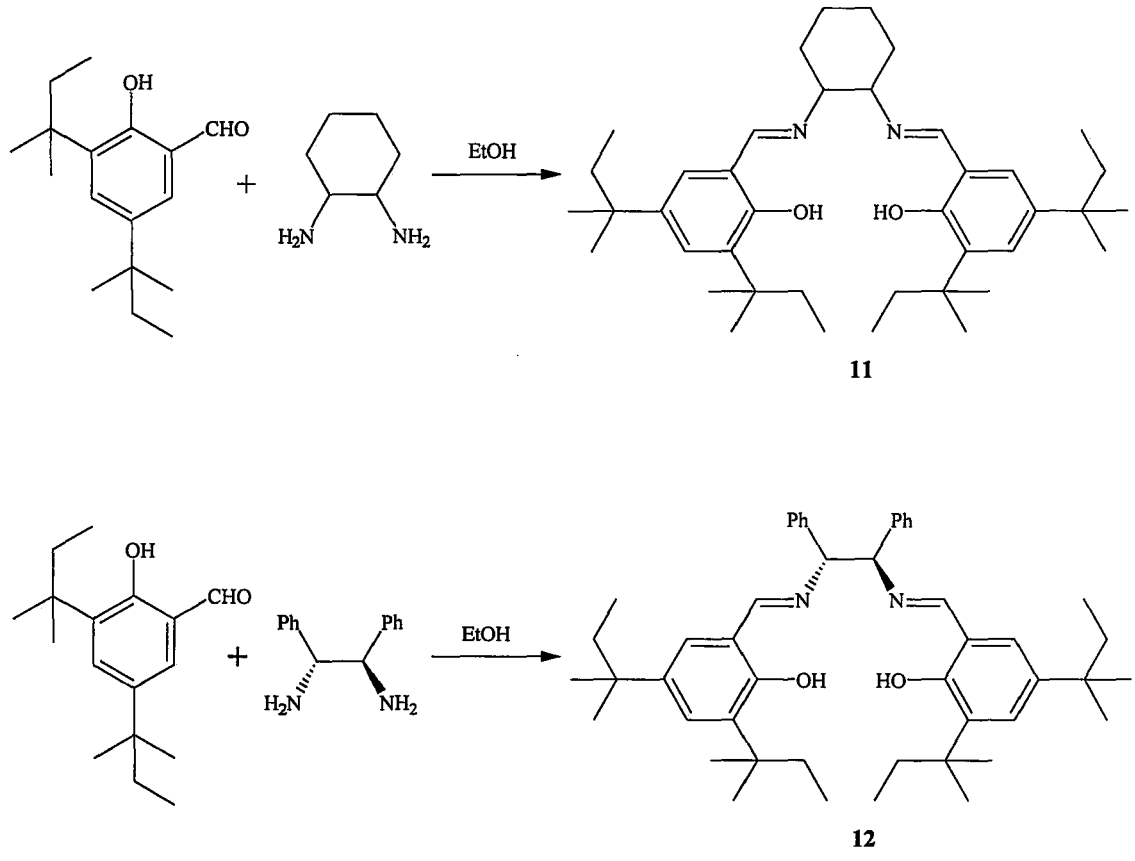


Figure 39: Reaction Schemes for the synthesis of the Schiff base ligands 11 and 12.

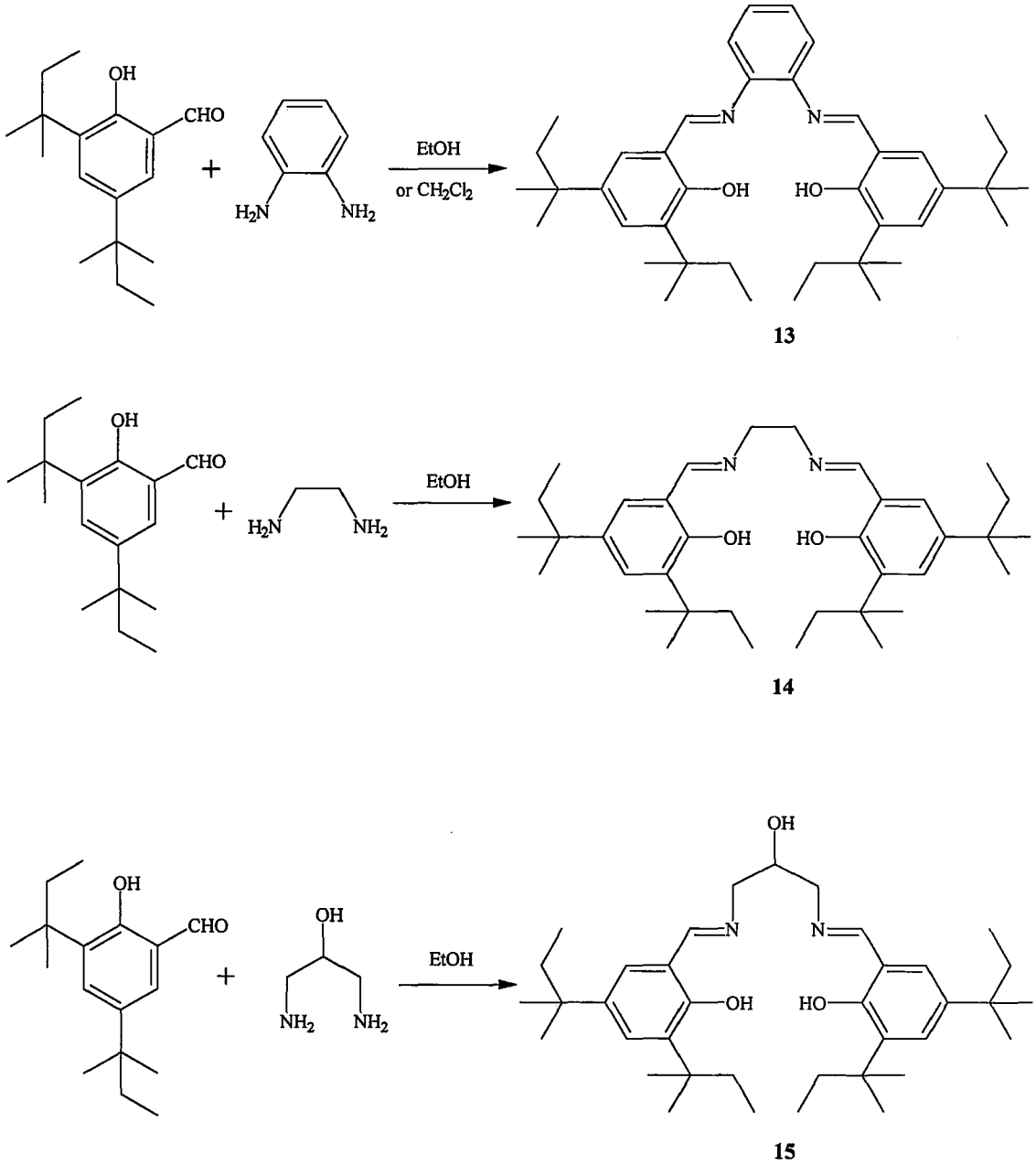


Figure 40: Reaction Schemes for the synthesis of the Schiff base ligands continued 13-15.

D. Metal Schiff Base Complexes

The ability of the Schiff base ligands to chelate with a variety of active metals is an important characteristic. The different active metal centers are the source of the salen metal complexes catalytic activity. A variety of monomeric Schiff base metal complexes were synthesized through the condensation of ligands **12-15** with various metal ions according to the Figure 39 and 40.

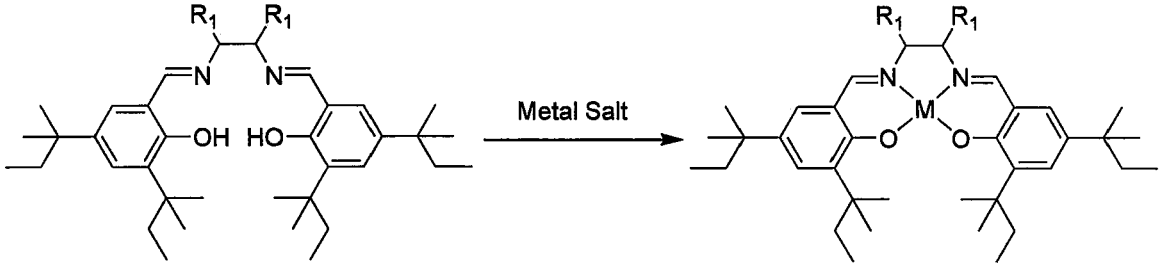


Figure 41: General reaction scheme for the synthesis of the Schiff base complexes.

Vanadyl complexes were prepared from the reaction of the ligand with $VO(acac)_2$ according to a reported method from our group.[64] The Fe(III) complex was prepared from the reaction of ferric chloride hexahydrate with the ligand.[65]

The treatment of the ligands with cupric acetate monohydrate at 40 °C for 2 hrs followed by continuous stirring overnight at r.t. gave Cu(II)salen complexes. The purification was done with recrystallization from ethyl acetate. The complexes are usually soluble in common organic solvents such as methylene chloride, chloroform,

benzene and acetone. Some of them are also soluble in non-polar solvents, such as hexane, because of the presence of *t*-pentyl groups.

Nickle(II) and Palladium(II) complexes were prepared from the reaction of the salen ligand derivatives with metal acetate or choride salts. Unlike Cu(II) complexes, these complexes are diamagnetic.

D.1. *Synthesis of the Fe(III) Complex from Ligand 11*

Ligand 11 was treated with ferric chloride in ethanol at reflux for 4 hrs to yield complex 16. The complex was purified by recrystallization from acetonitrile. Characterization by elemental analysis and IR confirmed the composition. Furthermore, we have obtained a high quality of crystals for the x-ray crystallography. In addition to the confirmation of the proposed structure, the x-ray determination revealed that the central geometry is pyramidal with Cl atom in the apical position. The crystallographic data are listed in Table 3. Selected bond distances and angles are listed in Table 4. Full bonding information (distances and angles) is provided in the Appendix section. The average Fe-O bond distance is 1.8835(20) Å while the average Fe-N bonding distance is 2.097(3) Å. The Fe-Cl bond length is 2.2436(11) Å. Another obvious fact is that all the ethyl groups are in the exo-relationship with Cl, meaning that Cl is located in the opposite direction to the ethyl group.

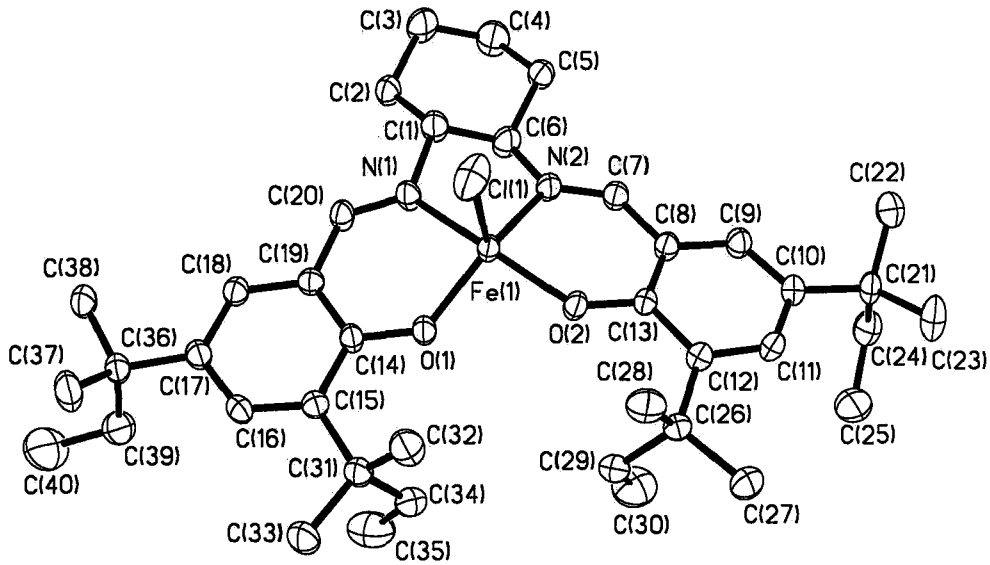


Figure 42. X-ray structure of (R,R) Chloro-(-)-[[*N,N'*-bis(3,5-di-*t*-pentylsalicylidene)-1, 2-cyclohexanediamine] – N, N', O, O'] ferric, complex, **(16)**

Table 3. Crystallographic data for adduct (**16**)

Empirical Formula	$C_{40}H_{60}ClFeN_2O_3$
Formula Weight	692.20
Temperature, *K*	153 (2)
Wavelength, Å	0.71073
Crystal system, space group	
a, Å	16.197(3)
b, Å	18.759(4)
c, Å	12.881(3)
α, β, γ, (deg)	90, 101.37(3), 90
Z	4
ρ_{calc}, mg/cm3	1.198
Crystal size, mm	0.36 x 0.19 x 0.14
Volume, $Å^3$	3837.0(13)
Theta range of data collection, deg	1.94 to 26.38
Reflection collection/unique	7835/6424 [R(int) =]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7835/0/455
Goodness-of-fit on F^2	1.107
Final R indices [I>2sigma(I)]	R_1 =0.0633 , R_w^2 =0.1524

Table 4. Selected bond distances (Å) and bond angle (deg) for adduct (**16**)

Fe(1)-O(1)	1.885 (2)	**O(2)-C(13)**	1.324 (3)
Fe(1)-O(2)	1.882 (2)	**N(1)-C(1)**	1.478 (4)
Fe(1)-N(1)	2.098 (2)	**N(1)-C(20)**	1.288 (4)
Fe(1)-N(2)	2.096 (3)	**N(2)-C(6)**	1.496 (4)
Fe(1)-Cl(1)	2.2436 (11)	**N(2)-C(7)**	1.299 (4)
O(1)-C(14)	1.326 (3)	**C(1)-C(6)**	1.510 (5)
C(14)-C(19)	1.416(4)	**C(8)-C(9)**	1.414(4)
C(8)-C(13)	1.413(4)	**C(19)-C(20)**	1.441(4)
O(2)-Fe(1)-O(1)	93.96 (9)	**N(1)-Fe(1)-N(2)**	77.28 (10)
O(2)-Fe(1)-N(1)	155.49 (10)	**O(2)-Fe(1)-Cl(1)**	105.85 (7)
O(1)-Fe(1)-N(1)	86.01 (9)	**O(1)-Fe(1)-Cl(1)**	111.29 (8)
O(2)-Fe(1)-N(2)	138.58 (10)	**N(1)-Fe(1)-Cl(1)**	96.90 (8)
O(1)-Fe(1)-N(2)	77.28 (10)	**N(2)-Fe(1)-Cl(1)**	108.18 (8)

D.2 *Synthesis of the Fe(III), VO(II), Pd(II), Cu(II) and Ni(II) Complexes from Ligand 12*

Ligand (**12**), prepared from the condensation of 1,2-diphenylethylenediamine with 3,5-di-t-pentylsalicylaldehyde, was used to reacted with the following metal salts: Ni(II) acetate, Cu(II) acetate, Pd(II) acetate, $VO(acac)_2$, and Fe(III) chloride. Compound (**12**) reacts with Ni(II) acetate, Cu(II) acetate, and Pd(II) acetate to afford Cu(Salen) (**17**), Ni(Salen) (**18**), and Pd(Salen) (**19**), respectively. The reaction with $VO(acac)_2$ is to give (VO)Salen (**20**). The reaction with Fe(III) chloride is to give (FeCl)(Salen) (**21**). The purification of the complexes is achieved by recrystallization. The complexes are fully characterized by elemental analysis, electronic spectroscopy, and FT-IR. For paramagnetic species such as Cu(Salen) and VO(Salen), ESR (electron spin resonance) spectra have been obtained to confirm the paramagnetic nature of the complexes. For diamagnetic species such as Ni(Salen) and Pd(Salen) complexes, the NMR spectra have been obtained to further support the structures.

Table 5. Transition-Metal Complexes from Ligand 12

Complex	Central metal	Color in solid state
17	Nickel(II)	Metallic-Brown
18	Cupric	Dark Metallic Green
19	Palladium(II)	Bright Yellow
20	Vanadium(IV) Oxide	Mint-Green
21	Ferric Chloride	Dark Metallic Purple

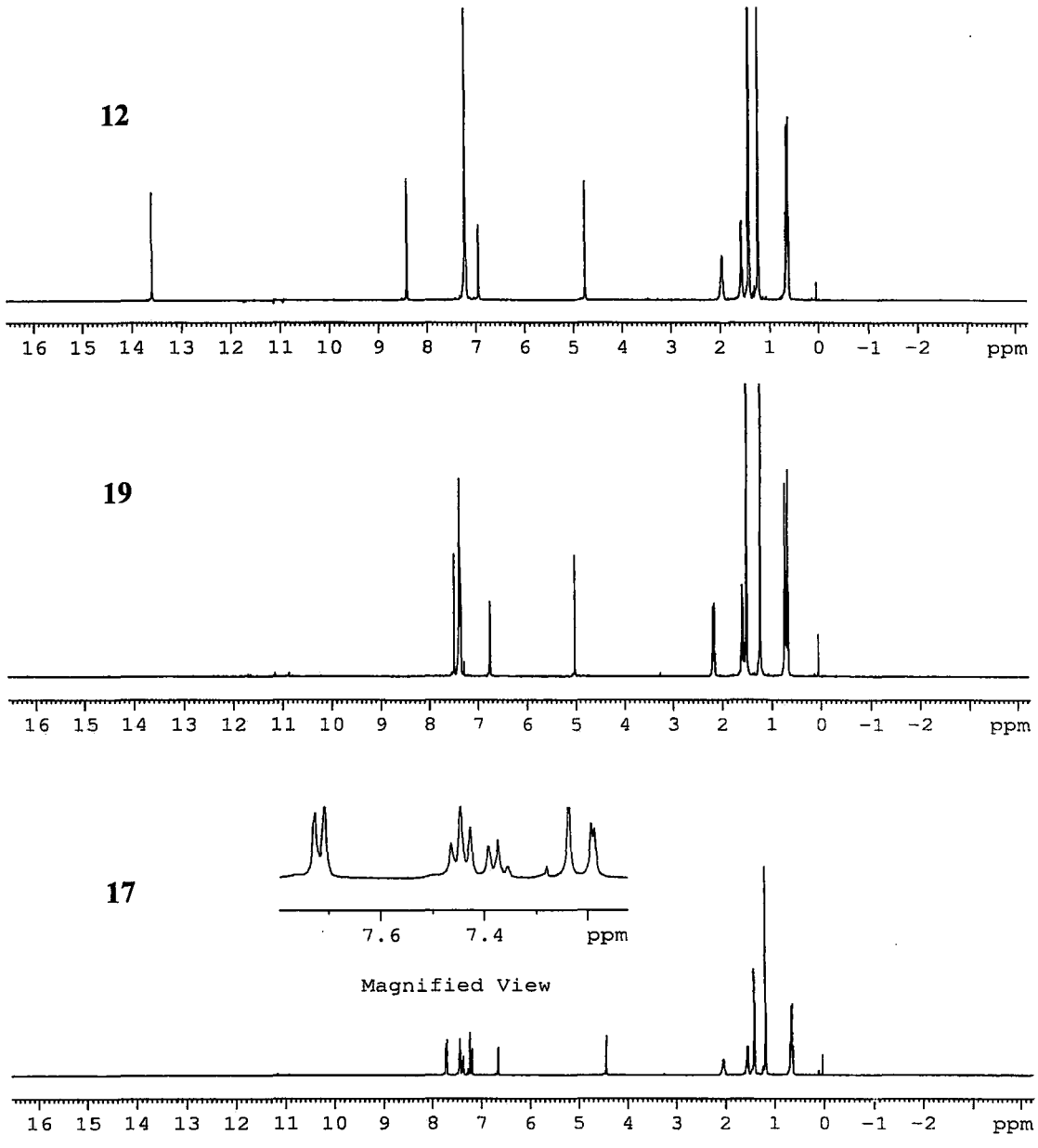


Figure 43. ^{1}H NMR spectra of the (R,R)-*N, N'*-Bis(3, 5-di-*t*-pentylsalicylidene)-1, 2-diphenylethylenediamine (**12**), (R,R)-(-)-[[*N,N'*-bis(3,5-di-*t*-pentylsalicylidene)-1, 2-diphenylethylenediamine] – N, N', O, O'] palladium(II) (**19**), and (R,R)-(-)-[[*N,N'*-bis(3,5-di-*t*-pentylsalicylidene)-1, 2-diphenylethylenediamine] – N, N', O, O'] nickel(II) (**17**).

The ligand (**12**) shows the OH proton signal at 13.53 ppm and imine proton signal at 8.36 ppm (Figure 38 a). Upon complexation, the OH proton signal disappears, in accordance with the deprotonation of OH for the coordination. The imine proton signal also undergoes dramatic changes since the nitrogen is involved in the coordination as well. For example, upon complexation with palladium, there is no OH proton signal between 13-14 ppm, indicative of the deprotonation of the OH group. The chemical shift of the imine proton moves to 7.48 ppm, a 0.88 ppm shift compared to that in the ligand (Figure 43, b). The same trend has been observed in complexation with Ni(II) (Figure 38, c).

D.3. *Synthesis of the Fe(III), VO(II), Cu(II), and Ni(II) Complexes from Ligand 13*

Ligand (**13**), which is prepared from the condensation of 1,2-diaminobenzene with 3,5-di-t-pentylsalicylaldehyde, has been found to react with various metal salts as well. A series of complexes have been obtained with the use of Ni(II) acetate, Cu(II) acetate, Pd(II) acetate, $VO(acac)_2$ (acac=acetylacetone), and Fe(III) chloride to react with (**13**). The reaction of (**13**) with Ni(II) acetate gives (**22**). The reaction with Cu(II) acetate yields (**23**). The reaction with $VO(acac)_2$ generates (**24**). The reaction with $FeCl_3$ leads to (**25**). All the complexes are purified by recrystallization, and characterized by elemental analysis, FT-IR, electronic spectroscopy, NMR (for diamagnetic species), and ESR (paramagnetic species).

Table 6. Transition-Metal Complexes from Ligand 13

Complex	Central metal	Color in solid state
22	Nickel(II)	Metallic Red-Brown
23	Copper(II)	Metallic Brown
24	Vanadium(IV) Oxide	Metallic Gold-Green
25	Iron(III)	Dark Metallic Purple

D.4. *Synthesis of the Fe(III), VO(II), Pd(II), Cu(II), and Ni(II) Complexes from Ligand 14*

Ligand (**14**) is prepared from the condensation of 1,2-ethylenediamine with 3,5-di-t-pentylsalicylaldehyde. The treatment of this ligand with various metal salts has led to the formation of a series of metal complexes. In this way, we have obtained Ni(salen) (**26**), Cu(Salen) (**27**), Pd(Salen) (**28**), VO(Salen) (**29**), and FeCl(Salen) (**30**).

Table 7. Transition-Metal Complexes from Ligand 14

Complex	Central metal	Color in solid state
26	Nickel(II)	Gold
27	Copper(II)	Dark Metallic Purple
28	Palladium(II)	Bright Yellow-Green
29	Vanadium(IV) Oxide	Metallic Forest Green
30	Iron(III)	Dark Metallic Purple

^{1}H NMR spectra show that the ligand has the OH proton signal at 13.69 ppm and the imine proton signal at 8.41 ppm. Upon the complexation, the OH proton signal is expected to disappear, and the imine proton signal is expected to shift upfield. These changes have been observed. An example is the case of palladium complexation (Figure 39). In Pd(II) complex (**18**), there was no peak between 13-14 ppm, indicating that the -OH proton disappeared due to the chelating action. The imine proton shifted to 7.69 ppm from 8.41 ppm.

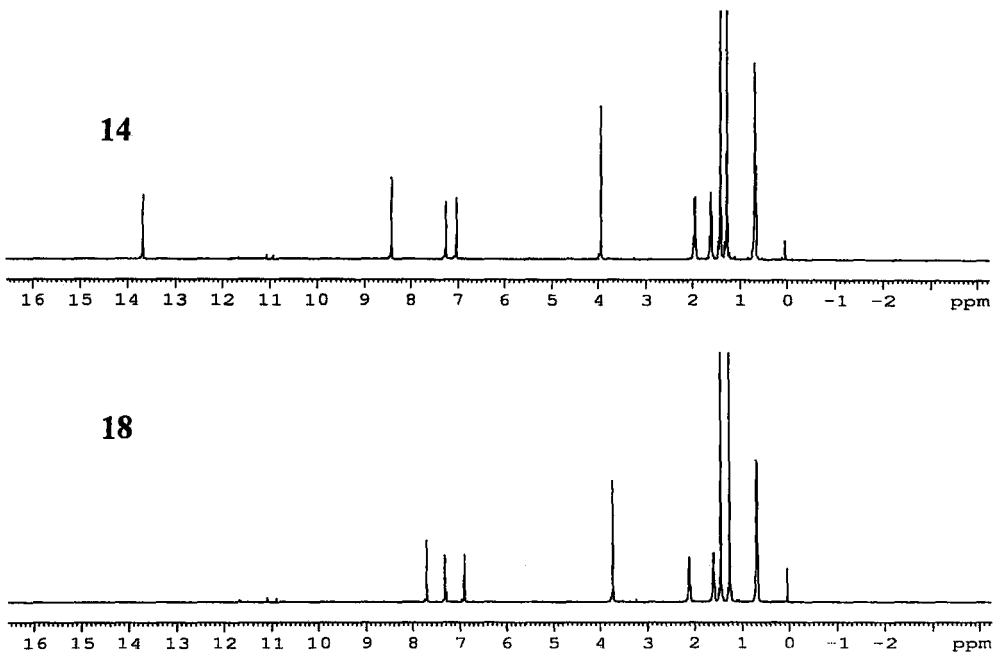


Figure 44. ^{1}H NMR spectra of the *N, N'*-Bis(3,5-di-*t*-pentylsalicylidene)-1, 2-ethylenediamine (**14**), and [[*N, N'*-Bis(3, 5-di-*t*-pentylsalicylidene)-1, 2-ethylenediamine] – N, N', O, O'] palladium (II) (**18**).

Other proton signals are not affected as much. For example, the ligand has the protons from salicylaldimine portion at 6.89 ppm and 7.31 ppm, respectively. Each is a singlet. The two *t*-pentyl groups at the 3- and 5- positions appeared in the range of 0.68 – 1.98 ppm, with two characteristic methyl groups, each with six protons, at 1.27 and 1.41 ppm, respectively. Two CH_3- groups from the CH_3CH_2- group of *t*-pentyl seem to overlap at 0.68 ppm. Ethylene from the diamine segment of the ligand appeared as a singlet at 3.93 ppm, suggesting the bis- Schiff base in solution state is rather symmetrical. Upon palladium complexation, only the ethylene peak showed a shift toward upfield. Such a shift is ascribed to the rigidity caused by the insertion of the metal in the ligand.

Complex (**20**) was further characterized by x-ray crystallography. Like complex (**16**), the central configuration around the metal is pyramidal with the Cl atom in the apical position. Other interesting structural features include (1) non-coplanarity between two planes: N1-C16-C15-C10-O1-Fe and N2-C3-C4-C9-O2-Fe; (2) ethylene segment (C1-C2) adopts a gauche configuration; and (3) all the ethyl groups (a total of four, two at the 3- position and the other two at the 5- position) have the exo-relationship with the Cl atom. The data collection parameters are listed in Table 8, and selected bonding distances and angles are listed in Table 9. Additional bonding distances and angles are provided in the Appendix. The average Fe-O bond distance is 1.874(5) Å, and the average Fe-N bond distance is 2.0815(6) Å. Clearly, the Fe-N bond is longer than that of Fe-O. The Fe-Cl bonding distance is 2.232 (2) Å. These values are found to be comparable to those from complex (**16**).

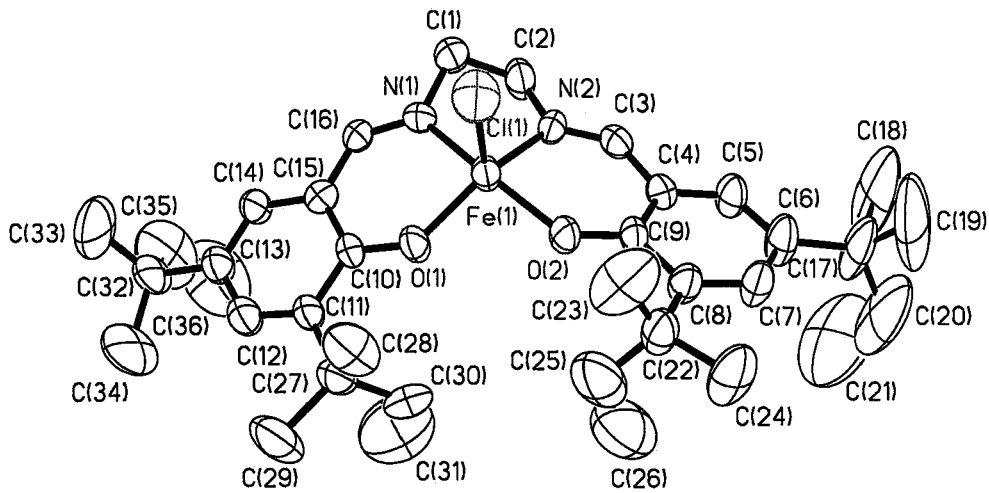


Figure 45. X-ray structure of Chloro-[[*N, N'*-Bis(3, 5-di-*t*-pentylsalicylidene)-1, 2-ethylenediamine] – N, N', O, O'] Iron (III) complex(**30**).

Table 8. Crystallographic Data for adduct **(30)**

Empirical Formula	$C_{36}H_{54}ClFeN_2O_2$
Formula Weight	638.12
Temperature, *K*	298 (2)
Wavelength, Å	0.71073
Crystal system, space group	
a, Å	9.1858(19)
b, Å	12.790(3)
c, Å	29.387(6)
$\alpha=\beta=\gamma$, (deg)	90
Z	4
ρ_{calc}, mg/cm3	1.177
Crystal size, mm	0.48 x 0.36 x 0.09
Volume, $Å^3$	3601.4(13)
Theta range of data collection, deg	2.54 to 25.01
Reflection collection/unique	4148/2815 [R(int) =]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4148/0/385
Goodness-of-fit on F^2	1.038
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0633$, $R_w^2 = 0.1908$

Table 9. Selected bond distances (Å) and bond angle (deg) for adduct **(30)**

Fe(1)-O(1)	1.870 (5)	**O(2)-C(9)**	1.301 (8)
Fe(1)-O(2)	1.878 (4)	**N(1)-C(1)**	1.452 (8)
Fe(1)-N(1)	2.076 (6)	**N(1)-C(16)**	1.301 (10)
Fe(1)-N(2)	2.087 (5)	**N(2)-C(2)**	1.454 (8)
Fe(1)-Cl(1)	2.232 (2)	**N(2)-C(3)**	1.273 (8)
O(1)-C(10)	1.304 (8)	**C(1)-C(2)**	1.492 (10)
C(15)-C(16)	1.408 (10)	**C(3)-(C4)**	1.453 (9)
C(10)-C(15)	1.443 (9)	**C(4)-(C9)**	1.403 (9)
O(1)-Fe(1)-O(2)	96.8 (2)	**N(1)-Fe(1)-N(2)**	75.4 (2)
O(1)-Fe(1)-N(1)	86.5 (2)	**O(1)-Fe(1)-Cl(1)**	111.06 (17)
O(2)-Fe(1)-N(1)	155.1 (2)	**O(2)-Fe(1)-Cl(1)**	104.62 (17)
O(1)-Fe(1)-N(2)	137.9 (2)	**N(1)-Fe(1)-Cl(1)**	97.15 (19)
O(2)-Fe(1)-N(2)	86.05 (19)	**N(2)-Fe(1)-Cl(1)**	108.67 (18)

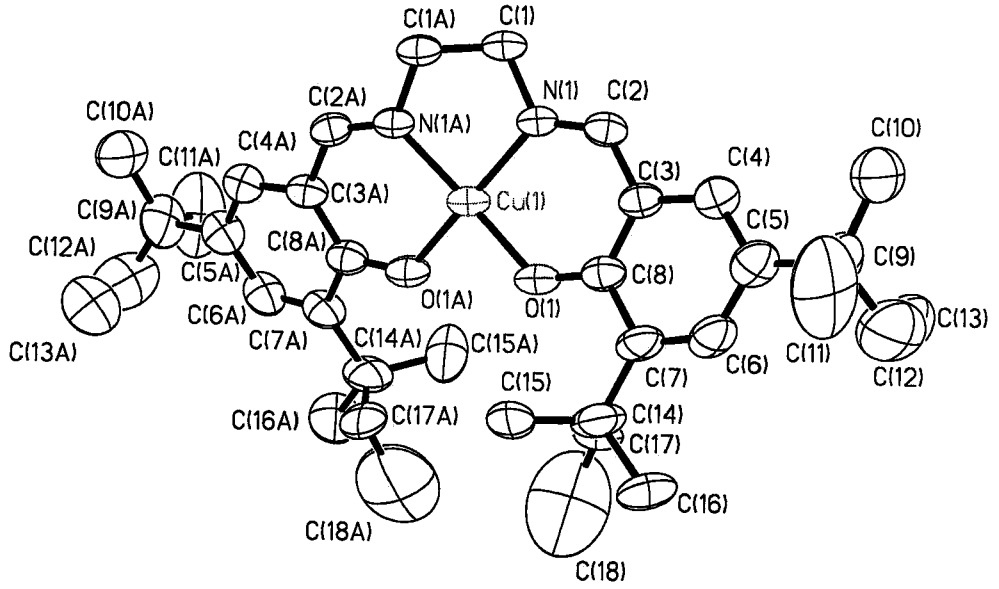


Figure 46. X-ray structure of racemic- Chloro-(-)-[[*N,N'*-bis(3,5-di-*t*-pentylsalicylidene)-1, 2-ethylenediamine] – N, N', O, O'] copper(II) complex, **(27)**

Table 10. Crystallographic Data for adduct **(27)**

Empirical Formula	$C_{36}H_{54}CuN_2O_2$
Formula Weight	610.35
Temperature, *K*	223 (2)
Wavelength, Å	0.71073
Crystal system, space group	Orthorhombic, Pbcn
a, Å	27.392(6)
b, Å	11.660(2)
c, Å	10.646(2)
$\alpha=\beta=\gamma$, (deg)	90
Z	4
ρ_{calc}, mg/cm3	1.192
Crystal size, mm	0.48 x 0.15 x 0.07
Volume, $Å^3$	3400.1(12)
Theta range of data collection, deg	2.54 to 25.01
Reflection collection/unique	3015/1939 [R(int) =]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3015/0/191
Goodness-of-fit on F^2	1.085
Final R indices [I>2 σ (I)]	$R_1 = 0.0938$, $R_w^2 = 0.3011$

Table 11: Selected bond distances (Å) and bond angle (deg) for adduct **(27)**

Cu(1)-O(1A)	1.882 (5)	**N(1A)-C(1A)**	1.483 (7)
Cu(1)-O(1)	1.882 (5)	**N(1A)-C(2A)**	1.278 (9)
Cu(1)-N(1A)	1.929 (5)	**N(1)-C(1)**	1.483 (7)
Cu(1)-N(1)	1.929 (5)	**N(1)-C(2)**	1.278 (9)
O(1A)-C(8A)	1.335 (9)	**C(1A)-C(1)**	1.519 (15)
C(3A)-C(2A)	1.420 (9)	**C(2)-C(3)**	1.420 (9)
C(8A)-C(3A)	1.412 (10)	**C(3)-C(8)**	1.412 (10)
O(1)-C(8)	1.335 (9)		
O(1)-Cu(1)-O(1A)	90.9 (3)	**N(1)-Cu(1)-N(2)**	85.4 (3)
O(1)-Cu(1)-N(1)	93.0 (2)		
O(1A)-Cu(1)-N(1)	168.3 (2)		
O(1)-Cu(1)-N(1A)	168.3 (2)		
O(1A)-Cu(1)-N(1A)	93.0 (2)		

D.5. *Synthesis of Fe(III), VO(II), Pd(II), and Cu(II) Complexes from Ligand 15*

The ligand (**15**) was prepared from the condensation of 1,3-Diamino-propan-2-ol with 3,5-di-t-pentylsalicylaldehyde.

Table 12. Transition-Metal Complexes from Ligand 15

Complex	Central metal	Color in solid state
31	Copper(II)	Metallic Forest Green
32	Palladium(II)	Bright Yellow-Gold
33	Vanadium(IV) Oxide	Dark Purple

CHAPTER IV

CONCLUSION

Five new series of transition-metal complexes, which could potentially serve as achiral or chiral salen catalyst for a variety of reactions, has been successfully synthesized and characterized. These complexes were synthesized from five different Schiff base systems derives from 3,5-Di-*t*-pentyl-2-hydroxybenzaldehyde (**2**).

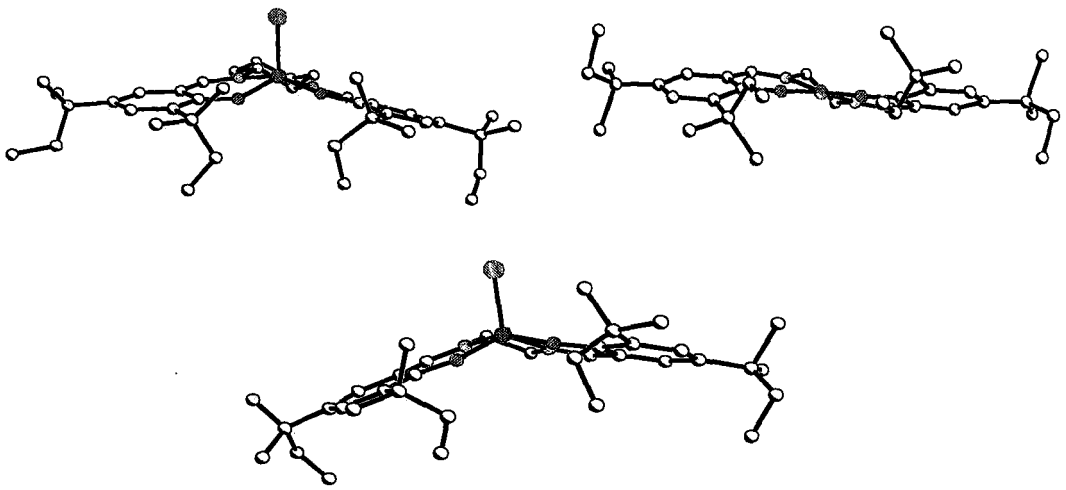


Figure 47. Side views of the X-ray structures of complexes (**16**), (**27**), and (**30**) respectively.

Also, three x-ray structures as shown above in Figure 47 of these complexes were obtained and studied for insight on the accessibility of the reactive site to substrate. It was concluded that the steric groups really build a wall-type function around three sides of the molecules: front and both sides. Also the *t*-pentyl groups takes care of up and bottom areas of the rim of a plane. It is observed that the ethyl group can go up and down to have rotations, which act as a steric force. From the observed it was concluded that access of a substrate to the active metal center has to be from the back side (Figue 48).

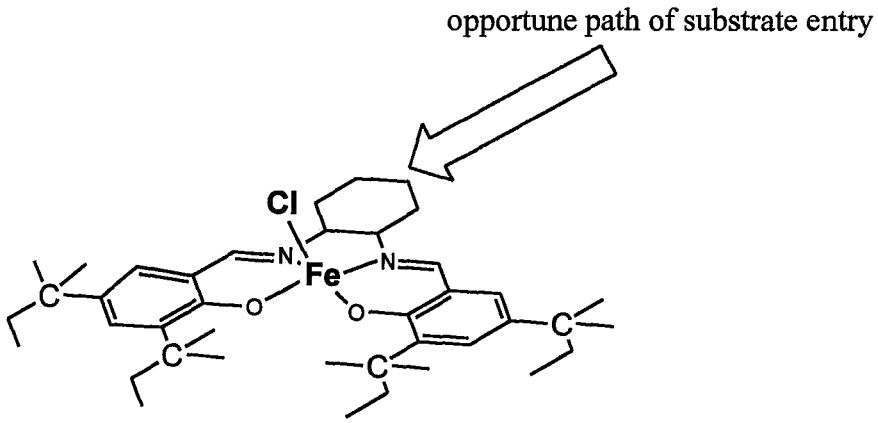


Figure 48. An ilistration of the substrate's only path of entry (the backside) for complex **(16)**.

It is projected that for Ph.D. research, these newly synthesized transition-metal catalysts will be evaluated in Asymmetrical Diels-Alder reactions. Also, more structural data from crystal x-ray will be obtained. Since it is now known that the only opportunity

the substrate has to access the active metal center is from the back side, this X-ray data will be used to determine what factor(s) will regulate the substrate's approach to the active metal center.

CHAPTER V

EXPERIMENTAL SECTION

General Experimental Procedures. All reactions were monitored by thin-layer chromatography (TLC). TLC plates were visualized with UV light. All yields reported refer to isolated material. Dry solvents used in these reactions were obtained as follows: Ethanol was distilled over magnesium churnings and iodine, and methylene chloride and toluene were dried over calcium hydride.

Column chromatography (Flash) purification was carried out using silica gel (32-63 μm particle size). Infrared (IR) spectra were recorded on an Omnic Impact 400 FT-IR spectrometer as thin films for oil and KBr pellets for solids. ^{1}H NMR (400MHz) and ^{13}C NMR (100.6 MHz) were recorded in $CDCl_3$ unless otherwise specified. Chemical shift values are expressed in ppm relative to tetramethylsilane (0.0 ppm) for ^{1}H and $CDCl_3$ (77.0ppm) for ^{13}C NMR. The enantiomeric excess was determined on a Shimadzu capillary GC-14A Ion Flame Detector with a Shimazu CR 501 Chromatopac integrator and chiral column (Chiraldex, 20m×0.25 mm ID×0.125 micro meter film). The oven temperature is about 100°C, and isothermal at 65 kPa. Optical rotation was obtained with a Rudolph Research Autopol III Digital Polarimeter in a thermostat cell at 20°C. All Elemental analysis was performed by Atlantic Microlab, Norcross, Ga.

3,5-Di-*t*-pentyl-2-hydroxybenzaldehyde (2). A 250 mL, three-necked, round-bottomed flask equipped with a stirred, an additional funnel, and a reflux condenser with nitrogen inlet was charged with 2,4-*tert*-pentylphenol (18.76 g, 80.0 mmol,1.0 equiv.) and 2,6-lutidine (3.72 g, 32.0 mmol, 0.8 equiv.) in 100mL of dry toluene. $SnCl_4$ (1.0 mL, 8.0 mmol, 0.2 equiv.) was added drop wise to the solution, and the addition funnel was rinsed with 3.0 mL of dry toluene to wash away the last traces of $SnCl_4$. The heterogeneous light yellow mixture was stirred at room temperature under nitrogen for 1 hr. Then, paraformaldehyde (7.94 g, 8.0 mmol, 0.2 equiv.) was quickly added as a solid. The mixture was heated at 100 °C in an oil bath. The mixture was allowed stirring for 12 hrs. The mixture was cooled to room temperature, and stirring was continued while 50 mL of water was added to the flask. The mixture was transferred to a separatory funnel (500 mL) and extracted with 3 100 mL portions of ethyl ether. The ethyl ether extracts were washed with 100 mL of water, 100 ml of brine and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure. The resulting oil was purified by flash chromatography using an 8.5:1.5 hexane/ethyl acetate solvent ratio. Typically, the yields were between 45-68%. IR: 3425, 2967, 2874, 2741, 1945, 1827, 1744, 1665, 1611, 1459, 1459 cm^{-1}. ^1H NMR ($CHCl_3$): δ (ppm): 0.63 (t, 3H J = 8 Hz, CH3), 0.68 (t, 3H, J = 8 Hz, CH3), 1.28 (s, 6H, CH3), 1.37 (s, 6H, CH3), 1.61 (q, 2H, CH2), 1.89 (q, 2H, CH2), 7.27 (d, 1H, J = 4 Hz, ArH), 7.45 (d, 1H, J = 4 Hz, ArH), 9.85

(s,1H, CHO), 11.61 (s, 1H, OH); ^{13}C NMR ($CHCl_3$): δ (ppm): 9.13, 9.48, 27.47, 28.41, 32.61, 36.80, 37.44, 38.67, 119.9, 128.8, 133.9, 139.8.

(R,R)-*N,N'*-Bis(3,5-di-*t*-pentylsalicylidene)-1, 2-cyclohexanediamine (11). This compound was previously prepared and published by Bu et al.[2]

(R,R)-*N, N'*-Bis(3, 5-di-*t*-pentylsalicylidene)-1, 2-diphenylethylenediamine (12). This compound was previously prepared and published by Bu et al.[66]

***N, N'*-Bis(3, 5-di-*t*-pentylsalicylidene)-1, 2-phenylenediamine (13).** 1,2-phenylenediamine (0.53g, 4.91mmol, 1.0 equiv.) was mixed with **(2)** (2.58g, 9.83mmol, 2.0equiv.), and anhydrous sodium sulfate (10 g) in ethanol (50 mL), and the mixture was stirred for 24 hrs at room temperature. The sodium sulfate was filtered off, and the solvent reduced under pressure to yield viscous yellowish-orange oil **(13)**; 1.87g (63.72 %). This oil was used without further purification.

***N, N'*-Bis(3,5-di-*t*-pentylsalicylidene)-1, 2-ethylenediamine (14). (2)** (1.66g, mmol, 2.0 equiv.) was mixed with 1,2-ethylenediamine (0.190g, mmol, 1.0 equiv.) in ethanol (30 mL), and the mixture was stirred for 16 hrs at room temperature. The reaction mixture was cooled to 0 °C, the precipitate was filtered and dried under reduced pressure. The precipitate was purified by recrystallization in ethanol to yield a crystalline yellow

powder **(14)**; 1.08g (62.2%). ^{1}H NMR (400 MHz, $CHCl_3$): δ (ppm): 0.68 (dt, J_2 = 7.37 Hz, J_1 = 1.37 Hz, 12H), 1.27 (s, 12H), 1.41 (s, 12H), 1.62 (q, J = 7.4 Hz, 4H), 1.98 (q, J = 7.4 Hz, 4H), 3.93 (s, 4H), 7.03 (d, J = 2.2 Hz, 2H), 7.26 (d, J = 2.1 Hz, 2H), 8.41 (s, 2H), 13.69 (s, 2H) ^{13}C NMR (100 MHz, $CHCl_3$): δ (ppm): 9.55, 9.94, 27.91, 28.90, 33.07, 37.31, 37.64, 38.98, 60.06, 118.06, 127.25, 129.43, 135.22, 138.52, 158.38, 168.12. Anal. Calcd for $C_{36}H_{56}N_2O_2$: C, 78.78; H, 10.28; N, 5.10. Found: C, 78.84; H, 10.32; N, 5.03.

***N, N'*-Bis(3, 5-di-*t*-pentylsalicylidene)- 1,3-Diamino-propan-2-ol (15).** 1,3-Diamino-propan-2-ol (0.43g, 4.75mmol,1.0 equiv.) was mixed with the **(2)** (2.49g, 9.49mmol,2.0 equiv.) in CH_2Cl_2 (50 mL), and the mixture was stirred for 12 hrs at room temperature. The reaction mixture was cooled to 0 C, the precipitate was filtered and dried under reduced pressure to yield a yellowish oil **(15)**, 2.12g (77.18 %). This oil was used without further purification. EI-GC data for this compound can be found in Appendix G.

Chloro-(R,R)-(-)-[[*N,N'*-bis(3,5-di-*t*-pentylsalicylidene)-1, 2-cyclohexanediamine] – N, N', O, O'] ferric, complex (16). In a 2-neck reaction flask shielded from light and purged with N_2, **(11)** (1.0 g, 1.66mmol, 1.0 equiv.) was dissolved in ethanol (10 mL) and ferric chloride hexahydrate (0.448 g, 1.66mmol, 1.0 equiv.) was

added. The reaction was heated at 40-45 C for 2 hrs followed by stirring for an additional 6 hrs at room temperature. The precipitate was filtered and dried under reduced pressure. The resulting brownish-purple powder was recrystallized in acetonitrile to yield **(36)**; 0.893 g (77.78 %). Anal. Calcd. for $C_{40}H_{60}ClFeN_2O_3$: C, 69.40; H, 8.74; N, 4.05. Found: C, 69.44; H, 8.83; N, 4.04.

(R,R)-(-)-[[*N,N'*-bis(3,5-di-*t*-pentylsalicylidene)-1, 2 diphenylethylenediamine] – N, N', O, O'] nickel (II), complex (17). Under N_2, **(2)** (0.40 g, 1.52 mmol, 2.0 equiv.), and 1,2-diphenylethylenediamine (0.1618 g, 0.76 mmol, 1.0 equiv.) was dissolved in (3:1) methylene chloride / EtOH (20mL) and refluxed for 2 hrs. The reaction mixture was cooled to room temperature followed by the addition of nickel(II) acetate tetrahydrate (0.190 g, 0.76 mmol, 1.0 equiv.) in 10.0ml of EtOH. The reaction was heated at reflux for 2 hrs followed by stirring for an additional 12 hrs at room temperature. The solvent was then removed under reduced pressure. The resulting brown powder was purified by flash column chromatography, (3:1) hexane/methylene chloride and (1:2) hexane/methylene chloride respectively to yield **(17)**, 0.38 g (65.79%) IR: 2961, 2873, 1611, 1528, 1455, 1433, 1381, 1326, 1301, 1242, 1173, 787, 699 cm^{-1}. ^1H NMR (400 MHz, $CHCl_3$): δ (ppm) : 0.65 (t, J = 7.5 Hz, 6H), 0.67 (t, J = 7.6 Hz, 6H). These two triples were overlapped, almost giving the appearance of a quartet, 1.18 (s, 12H), 1.41(d, J = 4.7 Hz, 12H), 1.55 (q, J = 7.4 Hz, 4H), 2.04 (q, J = 3.77 Hz, 4H), 4.44

(s, 2H), 6.65 (d, J = 2.3 Hz, 2H), 7.19 (d, J = 2.4 Hz, 2H), 7.23 (s, 2H), 7.37 (t, J = 7.3 Hz, 2H), 7.44 (t, J = 7.4 Hz, 4H) 7.71 (d, J = 7.3 Hz, 2H) ^{13}C NMR (100 MHz, $CHCl_3$): δ (ppm) : 9.58, 10.08, 28.02, 28.71, 32.64, 36.90, 37.26, 39.66, 79.66, 119.93, 127.47, 128.17, 128.99, 129.64, 131.74, 134.37, 138.84, 140.10, 163.76. Anal. Calcd for $C_{48}H_{62}N_2NiO_2$: C, 76.09; H, 8.25; N, 3.70. Found: C, 75.97; H, 8.23; N, 3.68.

(R,R)-(-)-[[*N,N'*-bis(3,5-di-*t*-pentylsalicylidene)-1, 2-diphenylethylenediamine] – N, N', O, O'] copper (II), complex (18). In a 2-neck reaction flask purged by N_2, **(2)** (1.18 g, 4.50 mmol, 2.0 equiv.), and 1,2-diphenylethylenediamine (0.477 g, 2.25 mmol, 1.0 equiv.) was dissolved in (3:1) methylene chloride / EtOH (20mL) and refluxed for 2 hrs. The reaction mixture was cooled to room temperature followed by the addition of cupric acetate monohydrate (0.45 g, 2.25 mmol, 1.0 equiv.) in 10.0ml of EtOH. The reaction was heated at reflux for 2 hrs followed by stirring for an additional 12 hrs at room temperature. The solvent was then removed under reduced pressure. The resulting greenish-blue powder was purified by flash column chromatography, (3:1) hexane/methylene chloride and (1:2) hexane/methylene chloride respectively to yield **(18)**, 0.38 g (65.79%). IR: 2960, 2873, 1610, 1526, 1456, 1430, 1382, 1241, 1166, 699, 532 cm $^{-1}$. Anal. Calcd. for $C_{48}H_{62}CuN_2O_2$: C, 75.60; H, 8.20; N, 3.67. Found: C, 75.42; H, 8.32; N, 3.66.

(R,R)-(-)-[[*N,N'*-bis(3,5-di-*t*-pentylsalicylidene)-1, 2-diphenylethylenediamine] – N, N', O, O'] palladium (II), complex (19). In a 2-neck reaction flask shielded from light and purged with N_2, **(2)** (0.40 g, 1.52 mmol, 2.0 equiv.), and 1,2-diphenylethylenediamine (0.1618 g, 0.76 mmol,1.0 equiv.) was dissolved in (3:1) methylene chloride / EtOH (20mL) and refluxed for 2 hrs. The reaction mixture was cooled to room temperature followed by the addition of palladium(II) acetate (0.171 g, 0.76 mmol, 1.0 equiv.) in 10.0ml of EtOH. The reaction was heated at reflux for 2 hrs followed by stirring for an additional 12 hrs at room temperature. The solvent was then removed under reduced pressure. The resulting bright yellow powder was purified by flash column chromatography, (3:1) hexane/methylene chloride and recrystallization in (3:1) methylene chloride / EtOH respectively to yield **(19)**, 0.356 g (58.0%) IR: 2960, 2873, 1609, 1523, 1454, 1429, 1381, 1324, 1300, 1237, 1164, 786, 699 cm^{-1}. ^1H NMR (400 MHz, $CHCl_3$): δ (ppm) : 0.66 (t, J = 8.9 Hz, 6H), 0.71 (t, J = 7.5 Hz, 6H), 1.20 (d, J = 3.0 Hz, 12H), 1.48 (s, 12H), 1.57 (q, J = 7.4 Hz, 4H), 2.16 (q, J = 7.4 Hz, 4H), 5.00 (s, 2H), 6.73 (d, J = 2.4 Hz, 2H), 7.34-7.40 (m, 12H) 7.48 (s, 2H) ^{13}C NMR (100 MHz, $CHCl_3$): δ (ppm) : . 9.60, 10.22, 27.95, 28.66, 28.82, 32.54, 36.98, 37.33, 39.93, 81.65, 120.09, 128.87, 129.31, 132.63, 134.92, 139.37, 161.02, 164.69. Anal. Calcd for $C_{48}H_{62}N_2O_2Pd$: C, 71.58; H, 7.76; N, 3.48. Found: C, 71.41; H, 7.58; N, 3.48.

(R,R)-(-)-[[*N,N'*-bis(3,5-di-*t*-pentylsalicylidene)-1, 2-diphenylethylenediamine] – N, N', O, O'] vanadium oxide, complex (20). (2) (0.515g, 1.96mmol, 2.0 equiv.), and 1,2-diphenylethylenediamine (0.208 g, 0.98mmol, 1.0 equiv.) was dissolved in ethanol (20mL) and refluxed for 2 hrs. The reaction mixture was cooled to room temperature followed by the addition of vanadyl acetylacetonate (0.260 g, 0.98mmol, 1.0 equiv.) in 10.0ml of methylene chloride. The reaction was heated at 40-45 °C for 2 hrs followed by stirring for an additional 6 hrs at room temperature. The precipitate was filtered and dried under reduced pressure. The complex was purified by column chromatography, (3:1) and (1:2) hexane/methylene chloride respectively to yield **(20)**, 0.107 g. IR: 2961, 2875, 1607, 1535, 1456, 1426, 1382, 1298, 1239, 1172, 980, 787, 730, 700, 576, 551 cm^{-1}. Anal. Calcd. For $C_{48}H_{62}N_2O_3V$ ¼ CH_2Cl_2: C, 73.62; H, 8.00; N, 3.56. Found: C, 73.94; H, 8.08; N, 3.63

Chloro-(R,R)-(-)-[[*N,N'*-bis(3,5-di-*t*-pentylsalicylidene)-1, 2-diphenylethylenediamine] – N, N', O, O'] ferric, complex (21). (2) (1.18 g, 4.50 mmol, 2.0 equiv.), and 1,2-diphenylethylenediamine (0.477 g, 2.25 mmol, 1.0 equiv.) was dissolved in methylene chloride (20mL) and refluxed for 2 hrs. The reaction mixture was cooled to room temperature followed by the addition of ferric chloride hexahydrate (0.608 g, 2.25 mmol, 1.0 equiv.) in 10.0ml of EtOH. The reaction was heated at reflux for 2 hrs followed by stirring for an additional 6 hrs at room temperature. The solvent

was then removed under reduced pressure. The resulting dark purple powder was purified by flash column chromatography, (3:1) hexane/methylene chloride and (1.5:1) methylene chloride/acetonitrile respectively to yield **(21)**, 1.09 g (61.34%). IR: 2963, 2875, 1606, 1537, 1456, 1429, 1384, 1295, 1238, 1166, 996, 699, 568 cm^{-1}. Anal. Calcd. For $C_{48}H_{62}ClFeN_2O_2$: C, 72.95; H, 7.91; N, 3.54. Found: C, 65.64; H, 7.03; N, 4.67.

[[*N, N'*-Bis(3, 5-di-*t*-pentylsalicylidene) -1, 2-phenylenediamine] – N, N', O, O'] nickel (II), complex (22). **(2)** (0.721 g, 2.75 mmol, 2.0 equiv.), and 1,2-phenylenediamine (0.1484 g, 1.37 mmol, 1.0 equiv.) was dissolved in chloroform (20mL) and refluxed for 2h. The reaction mixture was cooled to room temperature followed by the addition of nickel tetrahydrate (0.3414g, 1.37 mmol, 1.0 equiv.) in 10.0ml of EtOH. The reaction was heated to reflux for 24 hrs, followed by continuous stirring for an additional 30 minutes as the hotplate cooled down. The stirring was stopped, and the reaction flask was allowed to further cool with the hot plate for an additional 12 hrs and **(22)** precipitated out as metallic reddish-brown hair like crystals. The remaining mother liquor was reduced under pressure and recrystallized in (3:1) Chloroform / EtOH to yield a second portion of **(22)**. The two portions were combined to yield **(22)**, 0.5719 g, (63.77%). IR: 2959, 2872, 1610, 1582, 1523, 1460, 1428, 1370, 1173, 866, 784, 736, 587 cm^{-1}. ^1H NMR (400 MHz, $CHCl_3$): δ (ppm) : 0.65 (t, J = 7.4 Hz, 6H), 0.71 (t, J = 7.3 Hz, 6H), 1.29 (s, 12H), 1.42 (s, 12H), 1.64 (q, J = 7.3 Hz, 4H), 2.07 (q, J = 7.3 Hz, 4H),

7.05 (s, 2H), 7.19 (q, J = 3.1 Hz, 2H), 7.28 (d, J = 1.5 Hz, 2H), 7.70 (q, J = 3.1 Hz, 2H), 8.23 (s, 2H), ^{13}C NMR (100 MHz, $CHCl_3$): δ (ppm) : 9.61, 10.03, 28.15, 28.69, 32.65, 36.89, 39.77, 114.79, 119.77, 126.87, 128.10, 133.00, 135.34, 139.20, 143.31, 154.56, 165.35. Anal. Calcd. for $C_{40}H_{54}N_2NiO_2$: C, 73.51; H, 8.33; N, 4.29. Found: C, 73.52; H, 8.37; N, 4.34.

[[*N, N'*-Bis(3, 5-di-*t*-pentylsalicylidene) -1, 2-phenylenediamine] – N, N', O, O'] copper (II), complex (23). (13) (2.2 g, 3.7 mmol, 1.0 equiv.) was dissolved in ethanol (30 mL) and copper(II) acetate monohydrate (0.736 g, 3.7 mmol, 1.0 equiv.) was added. The reaction was heated at 40-45 °C for 2 hrs followed by stirring for an additional 8 hrs at room temperature. The precipitate was filtered and dried under reduced pressure. The resulting precipitate was recrystallized in EtOAc to give pure **(23)**; yield 2.36 g (97.25%). IR: 2960, 2874, 1605, 1580, 1558, 1523, 1488, 1459, 1432, 1381, 1175, 741 cm $^{-1}$. Anal. Calcd. for $C_{40}H_{54}CuN_2O_2$: C, 72.97; H, 8.27; N, 4.25. Found: C, 72.92; H, 8.22; N, 4.38.

[[*N, N'*-Bis(3, 5-di-*t*-pentylsalicylidene) -1, 2-phenylenediamine] – N, N', O, O'] vanadium oxide, complex (24). (2) (2.00 g, 7.62 mmol, 2.0 equiv.), and 1,2-phenylenediamine (0.412 g, 3.81 mmol, 1.0 equiv.) was dissolved in methylene chloride (50mL) and refluxed for 2 hrs. The reaction mixture was cooled to room temperature

followed by the addition of vanadyl acetylacetonate (1.01 g, 3.81 mmol, 1.0 equiv.) in 10.0ml of methylene chloride. The reaction was heated to reflux for 24 hrs. The solvent was removed under reduced pressure and then purified by flash column (3:1) hexane/methylene chloride and (1:2) hexane/methylene chloride respectively **(24)**, 2.23 g, (88.41%). IR: 2961, 2874, 1603, 1579, 1531, 1459, 1424, 1381, 1360, 1179, 986, 747, 554 cm^{-1}. Anal. Calcd. for $C_{40}H_{54}N_2O_3V$: C, 72.59; H, 8.22; N, 4.23. Found: C, 72.68; H, 8.29; N, 4.25.

Chloro-[[*N, N'*-Bis(3, 5-di-*t*-pentylsalicylidene) -1, 2-phenylenediamine] – N, N', O, O'] ferric, complex (25). **(2)** (0.721 g, 2.75 mmol, 2.0 equiv.), and 1,2-phenylenediamine (0.1484 g, 1.37 mmol, 1.0 equiv.) was dissolved in chloroform (20mL) and refluxed for 2 hrs. The reaction mixture was cooled to room temperature followed by the addition of ferric chloride hexahydrate (0.3709 g, 1.37 mmol, 1.0 equiv.) in 10.0ml of ethanol. The reaction was heated to reflux for 24 hrs, followed by continuous stirring for an additional 30 minutes as the hotplate cooled down. The stirring was stopped, and the reaction flask was allowed to further cool with the hot plate for an additional 12 hrs and **(25)** precipitated out as very dark purple hair like crystals. The remaining mother liquor was reduced under pressure and recrystallized in acetonitrile to yield a second portion of **(25)**. The two portions were combined to yield **(25)**, 0.6440 g, (68.39%). IR: 2962, 2873, 1602, 1578, 1558, 1531, 1459, 1424, 1381, 1358, 1301, 1178, 746, 554, 537 cm^{-1}.

Anal. Calcd for $C_{40}H_{54}ClFeN_2O_2$: C, 70.02; H, 7.93; N, 4.08. Found: C, 69.80; H, 7.81; N, 4.19.

[[*N, N'*-Bis(3, 5-di-*t*-pentylsalicylidene) -1, 2-ethylenediamine] – N, N', O, O'] nickel (II), complex (26). (14) (0.6 g, 1.09 mmol, 1.0 equiv.) was dissolved in ethanol (10 mL) and nickel(II) acetate tetrahydrate (0.272 g, 1.09 mmol, 1.0 equiv.) was added. The reaction was heated at 40-45 °C for 2 hrs followed by stirring for an additional 6 hrs at room temperature. The precipitate was filtered and dried under reduced pressure. The complex was purified by column chromatography to give pure **(26)**; yield 0.6459 g (97.57%). IR: 2961, 2873, 1614, 1531, 1441, 1442, 1334, 1381, 1303, 1238, 1171, 786, 540 cm^{-1}. ^1H NMR (400 MHz, $CHCl_3$): δ (ppm) : 0.59 - 0.66 (m, 12H), 1.21 (s, 12H), 1.34 (s, 12H), 1.58 (s, H2O), 1.53 - 1.57 (m, 4H), 1.97 (q, J = 6.9 Hz, 4H), 3.30 (s, 4H), 6.79 (s, 2H), 7.15 (s, 2H), 7.47 (s, 2H),: Anal. Calcd. for $C_{36}H_{54}N_2NiO_2$: C, 71.41; H, 8.99; N, 4.63. Found: C, 70.84; H, 9.01; N, 4.59.

[[*N, N'*-Bis(3, 5-di-*t*-pentylsalicylidene) -1, 2-ethylenediamine] – N, N', O, O'] copper (II), complex (27). (14) (0.6 g, 1.09 mmol, 1.0 equiv.) was dissolved in ethanol (10 mL) and copper(II) acetate monohydrate (0.218 g, 1.09 mmol, 1.0 equiv.) was added. The reaction was heated at 40-45 °C for 2 hrs followed by stirring for an additional 6 hrs at room temperature. The precipitate was filtered and dried under reduced pressure. The

complex was purified by column chromatography to give pure **(27)**; yield 0.6190g (92.77%). IR: 2961, 2874, 1619, 1529, 1440, 1412, 1384, 1334, 1301, 1237, 1165, 790 cm^{-1}. Anal. Calcd for $C_{36}H_{54}CuN_2O_2$: C, 70.84; H, 8.92; N, 4.59. Found: C, 70.74; H, 9.01; N, 4.46.

[[*N, N'*-Bis(3, 5-di-*t*-pentylsalicylidene) -1, 2-ethylenediamine] – N, N', O, O'] palladium (II), complex (28). In a 2-neck reaction flask shielded from light and purged with nitrogen, **(14)** (0.6 g, 1.09 mmol, 1.0 equiv.) was dissolved in ethanol (10 mL) and palladium (II) acetate (0.25 g, 1.09 mmol, 1.0 equiv.) was added. The reaction was heated at 40-45 °C for 2 hrs followed by stirring for an additional 6 hrs at room temperature. The precipitate was filtered and dried under reduced pressure. The complex was purified by column chromatography to give pure **(28)**; yield 0.427 g (59.79 %). IR: 2961, 2874, 1614, 1612, 1526, 1455, 1434, 1383, 1331, 1300, 1235, 1163, 784 cm^{-1}. ^1H NMR (400 MHz, $CHCl_3$): δ (ppm) : 0.67 (t, J = 7.1 Hz, 12H), 1.25 (s, 12H), 1.44 (s, 12H), 1.59 (q, J = 7.4 Hz, 4H), 2.10 (q, J = 7.5 Hz, 4H), 3.72 (s, 4H), 6.89 (d, J = 2.4 Hz, 2H), 7.31 (d, J = 2.4 Hz, 2H), 7.69 (s, 2H), ^{13}C NMR (100 MHz, $CHCl_3$): δ (ppm) : 9.61, 10.22, 27.93, 28.78, 32.42, 37.10, 37.32, 39.88, 60.08, 120.00, 128.91, 132.31, 134.10, 139.26, 160.34, 164.38. Anal. Calcd. for $C_{36}H_{54}N_2O_2Pd$: C, 66.19; H, 8.33; N, 4.29. Found: C, 66.12; H, 8.41; N, 4.28.

[[*N, N'*-Bis(3, 5-di-*t*-pentylsalicylidene) -1, 2-ethylenediamine] – N, N', O, O'] vanadium oxide, complex (29). (14) (0.6 g, 1.09 mmol, 1.0 equiv.) was dissolved in ethanol (10 mL), and vanadyl acetylacetonate (0.30g, 1.09mmol, 1.0 equiv.) was added. The reaction was heated at 40-45 °C for 2 hrs followed by stirring for an additional 6 hrs at room temperature. The precipitate was filtered and dried under reduced pressure. The complex was purified by flash column chromatography, (3:1) hexane/methylene chloride to yield **(29)**, 0.536 g. (79.88%) IR: 2962, 2874, 1616, 1536, 1442, 1413, 1384, 1360, 1334, 1296, 1236, 1217, 1169, 977, 788, 732, 543 cm^{-1}. Anal. Calcd. for $C_{36}H_{54}N_2O_3V$ ¾ CH_2Cl_2: C, 65.15; H, 8.25; N, 4.135. Found: C, 64.84; H, 8.42; N, 4.17.

Chloro-[[*N, N'*-Bis(3, 5-di-*t*-pentylsalicylidene) -1, 2-ethylenediamine] – N, N', O, O'] ferric, complex (30). (14) (6.0 g, 1.09 mmol, 1.0 equiv.) was dissolved in ethanol (10 mL), and Ferric Chloride (0.295g, 1.09 mmol, 1.0 equiv.) was added. The reaction was heated at 40-45 °C for 2 hrs followed by stirring for an additional 6 hrs at room temperature. The precipitate was filtered and dried under reduced pressure, then purified by flash column (3:1) hexane/methylene chloride and (3:1) methylene chloride/acetonitrile, respectively. The resulting complex was further purified by recrystallization in acetonitrile to yield **(30)**, 0.549 g (78.70%). IR: 2962, 2873, 1612, 1538, 1440, 1413, 1384, 1292, 1236, 541 cm^{-1}. Anal. Calcd. for $C_{36}H_{54}ClFeN_2O_2$: C, 67.76; H, 8.53; N, 4.39. Found: C, 67.76; H, 8.50; N, 4.39.

[[*N, N'*-Bis(3, 5-di-*t*-pentylsalicylidene) -1,3-Diamino-propan-2-ol] – N, N', O, O'] copper (II), complex (31). **(2)** (0.250 g, 0.95 mmol, 2.0 equiv.), and 1,3-diamino-propan-2-ol (0.043 g, 0.48 mmol, 1.0 equiv.) was dissolved in EtOH (20mL) and refluxed for 2 hrs. The reaction mixture was cooled to room temperature followed by the addition of cupric(II) acetate monohydrate (0.095g, 0.48 mmol, 1.0 equiv.) in 10.0ml of EtOH. The reaction was heated to reflux for 2 hrs, followed by continuous stirring for 6 hrs at r.t. The solvent was removed under reduced pressure, and the resulting powder was recrystallized in (2:1) chloroform / EtOAc to yield **(31)**, 0.226 g, (74.08%). IR: 2960, 2874, 1618, 1530, 1438, 1411, 1382, 1360, 1323, 1296, 1234, 1167, 630 cm^{-1}. Anal. Calcd. for $C_{37}H_{56}CuN_2O_3$: C, 69.39; H, 8.81; N, 4.37. Found: C, 69.29; H, 9.03; N, 4.32.

[[*N, N'*-Bis(3, 5-di-*t*-pentylsalicylidene) -1,3-Diamino-propan-2-ol] – N, N', O, O'] palladium (II), complex (32). In a 2-neck reaction flask shielded from light and purged with N_2, **(2)** (1.0 g, 3.81 mmol, 2.0 equiv.) and 1,3-diamino-propan-2-ol (0.1717 g, 1.91 mmol, 1.0 equiv.) was dissolved in EtOH (30mL) and refluxed for 2 hrs. The reaction mixture was cooled to room temperature followed by the addition of palladium(II) acetate (0.428 g, 1.91 mmol, 1.0 equiv.) in 20.0ml of EtOH. The reaction was heated to reflux for 2 hrs, followed by continuous stirring for 6 hrs at r.t. The solvent was removed under reduced pressure, and the resulting powder was purified by silica gel

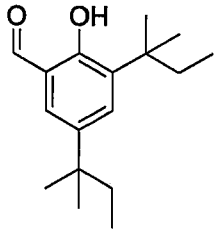
flash chromatography with methylene chloride as an eluent to yield **(32)**, 0.872g, (66.97%). IR: 2960, 2874, 1612, 1533, 1456, 1436, 1413, 1380, 1322, 1303, 1235, 1169, 1053 cm^{-1}. ^1H NMR (400 MHz, $CHCl_3$): δ (ppm) : 0.63 (t, J = 7.4 Hz, 6H), 0.68 (t, J = 7.4 Hz, 6H), 1.23 (d, J = 3.5 Hz, 12H), 1.43 (s, 12H), 1.587 (s, H_2O), 1.591(q, J = 7.4 Hz, 4H), 2.07 (q, J = 7.4 Hz, 4H), 2.69 (d, J = 10.39 Hz, -OH), 3.57 (d, J = 5.4 Hz, 1H), 3.61 (d, J = 5.3 Hz, 1H), 3.94 (d, J = 13.8 Hz, 2H), 3.92-4.12 (m, -CH) *proton bridge-head carbon*, 6.81 (d, J = 2.4 Hz, 2H), 7.28 (d, J = 2.4 Hz, 2H), 7.55 (s, 2H), ^{13}C NMR (100 MHz, $CHCl_3$): δ (ppm) : 9.61, 10.09, 28.37, 28.41, 28.68, 28.75, 32.81, 36.99, 37.29, 39.83, 64.75, 67.10, 119.13, 129.30, 133.36, 134.54, 138.01, 163.43, 166.39. Anal. Calcd. for $C_{37}H_{56}N_2O_3Pd$: C, 65.04; H, 8.26; N, 4.10. Found: C, 65.17; H, 8.31; N, 4.06.

[[*N, N'*-Bis(3, 5-di-*t*-pentylsalicylidene) -1,3-Diamino-propan-2-ol] – N, N', O, O'] vanadium oxide, complex. (33) In a 2-neck reaction flask shielded from light and purged with N_2, **(2)** (0.25g, 0.95 mmol, 2.0 equiv.) and 1,3-diamino-propan-2-ol (0.04g, 0.48 mmol, 1.0 equiv.) was dissolved in EtOH (30mL) and refluxed for 2 hrs. The reaction mixture was cooled to room temperature followed by the addition of vanadyl acetylacetonate (0.13g, 0.48mmol, 1.0 equiv.) in 20.0ml of EtOH. The reaction was heated to reflux for 2 hrs, followed by continuous stirring for 6 hrs at r.t. The solvent was removed under reduced pressure, and the resulting powder was purified by silica gel flash

chromatography to yield viscous purple oil **(33),** 0.21g, (73.68%). EI-GC data for this compound can be found in Appendix X.

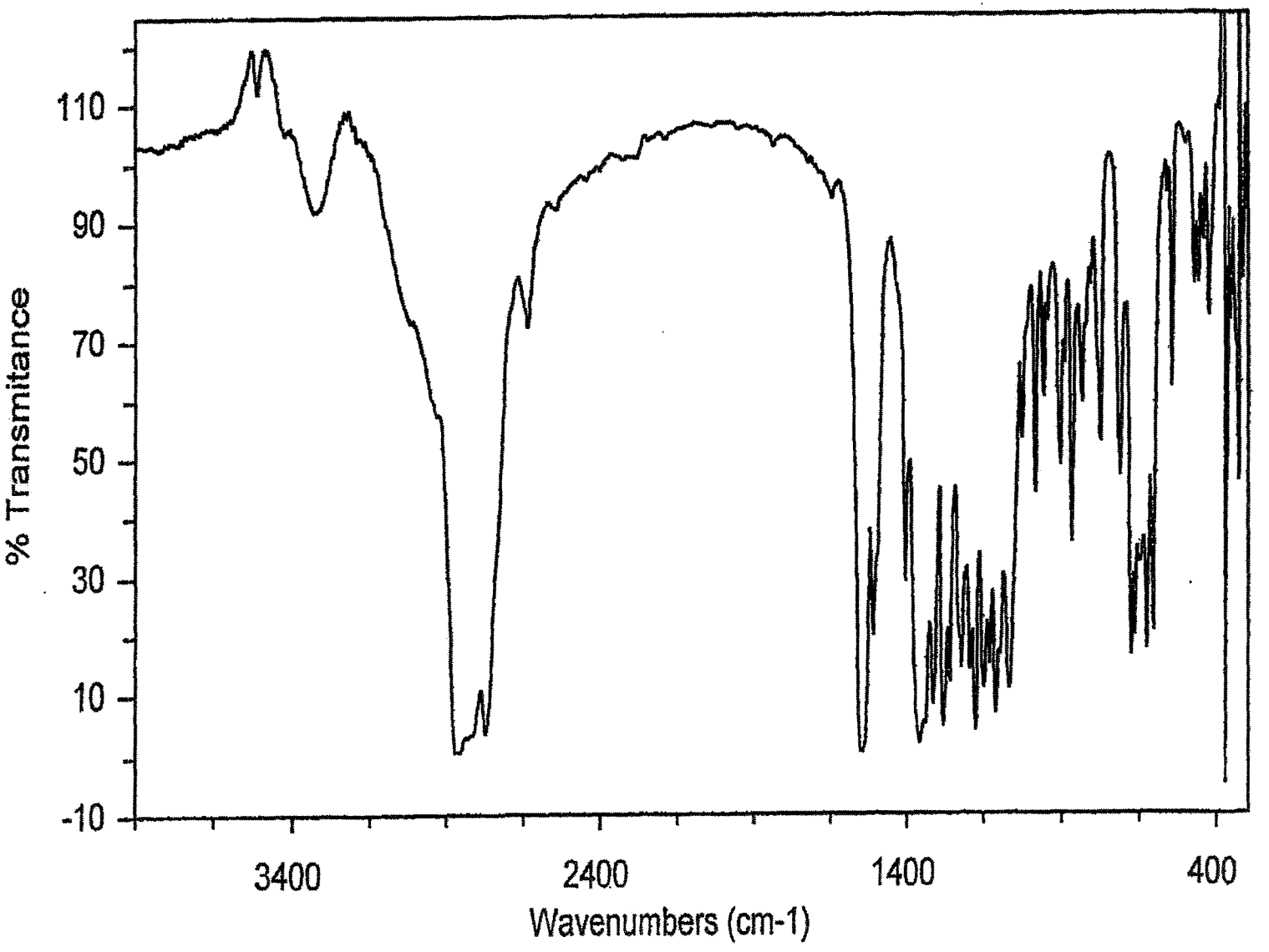
Appendix A

3,5-di-*t*-Pentyl-2-hydroxybenzaldehyde



(2)

^{1}H NMR
^{13}C NMR
FT-IR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50
30
10
-10
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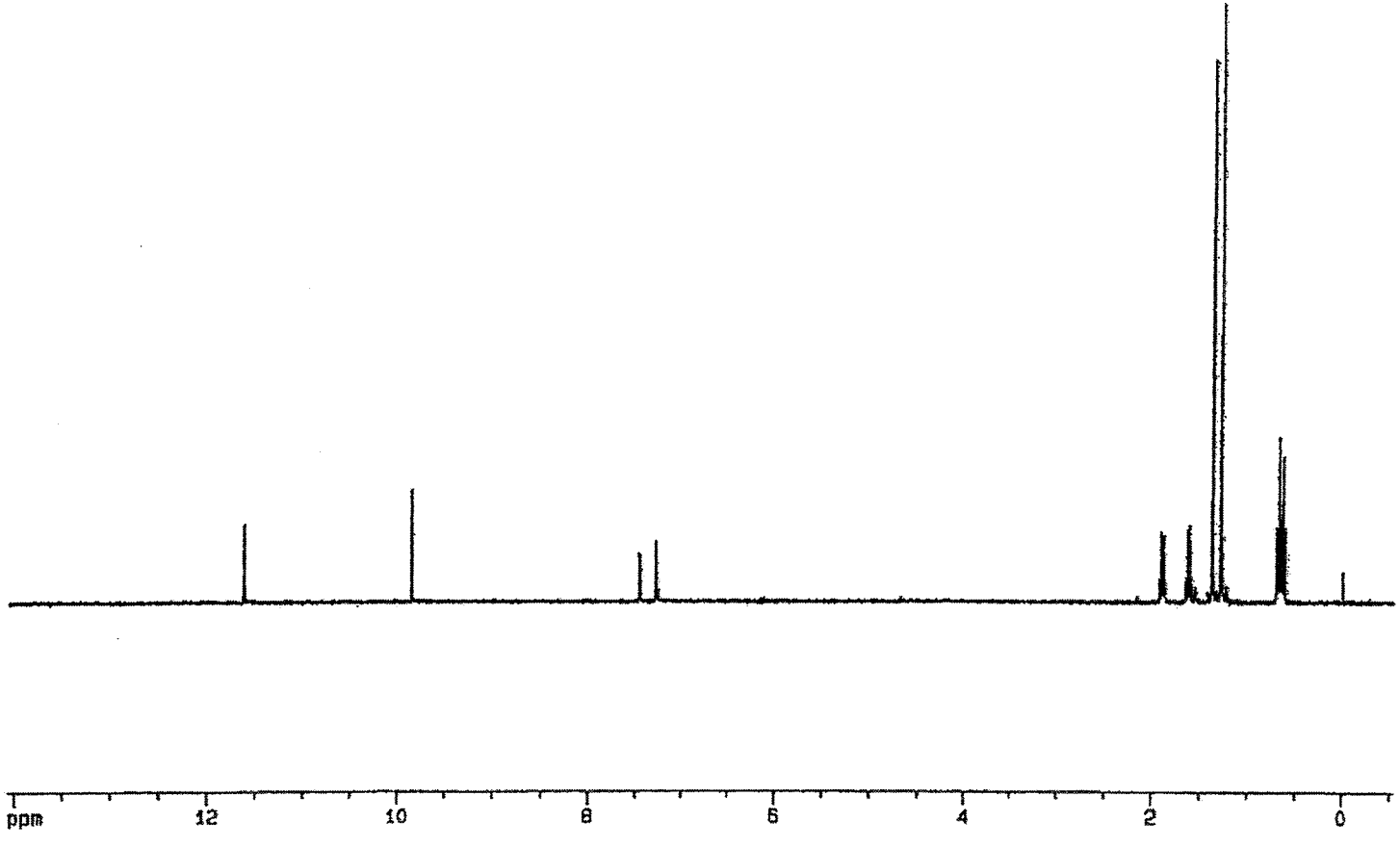
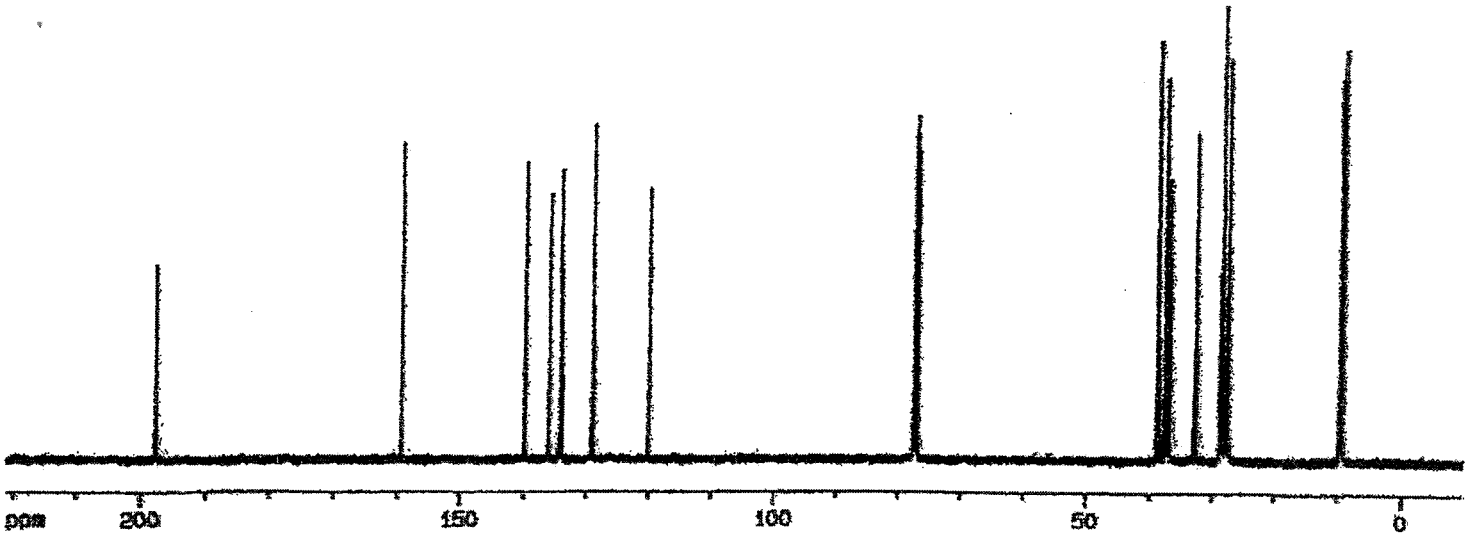
3400
2400
1400
400
Wavenumbers (cm-1)



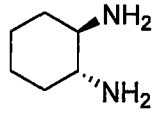
^{1}H NMR spectrum ($CDCl_3$/TMS) of 3, 5-*tert*-pentyl-2-hydroxybenzaldehyde



^{13}C NMR spectrum ($CDCl_3$/TMS) of 3, 5-*tert*-pentyl-2-hydroxybenzaldehyde

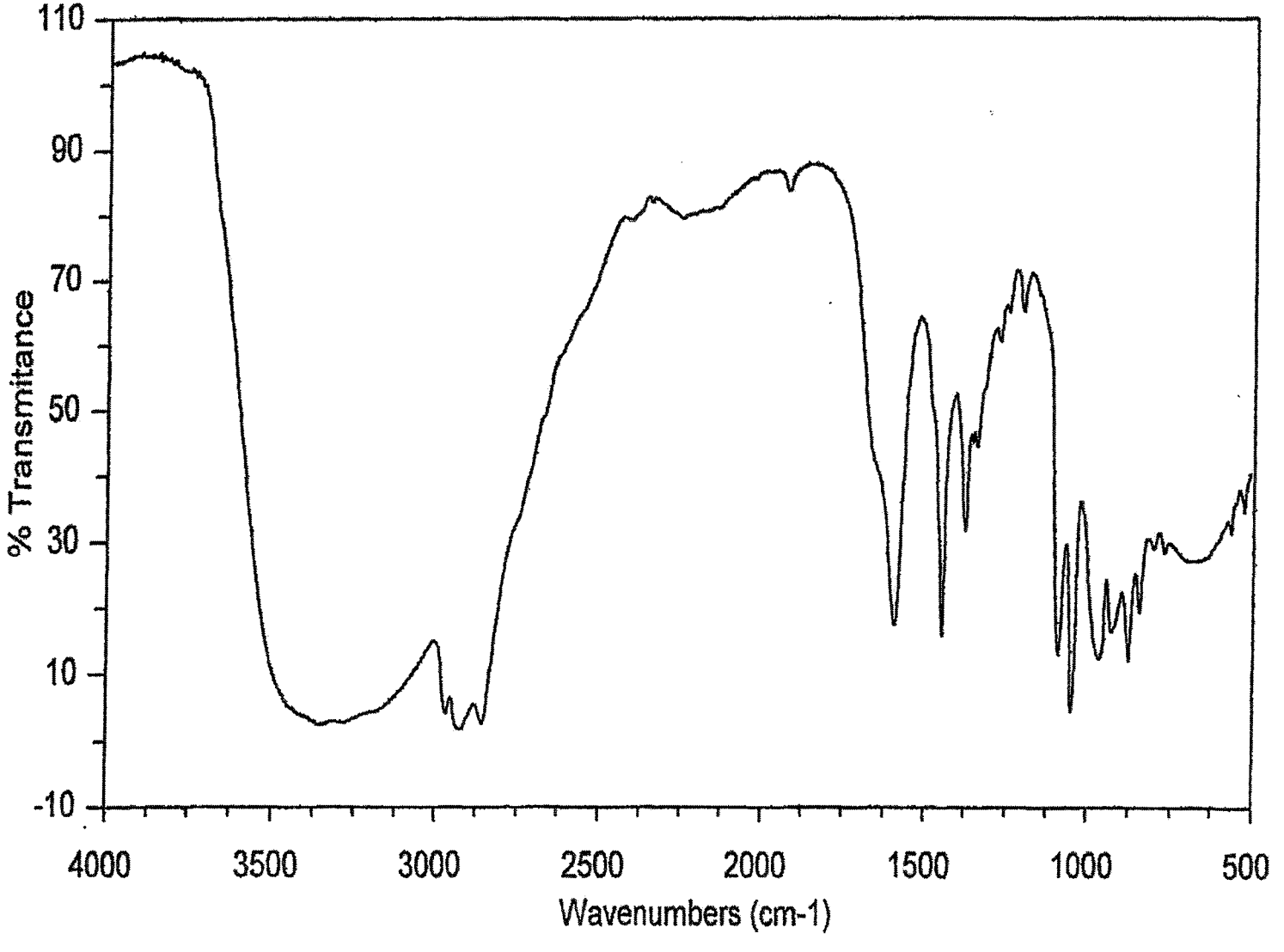
Appendix B

1,2-Cyclohexanediamine



(7)

^{1}H NMR
^{13}C NMR
FT-IR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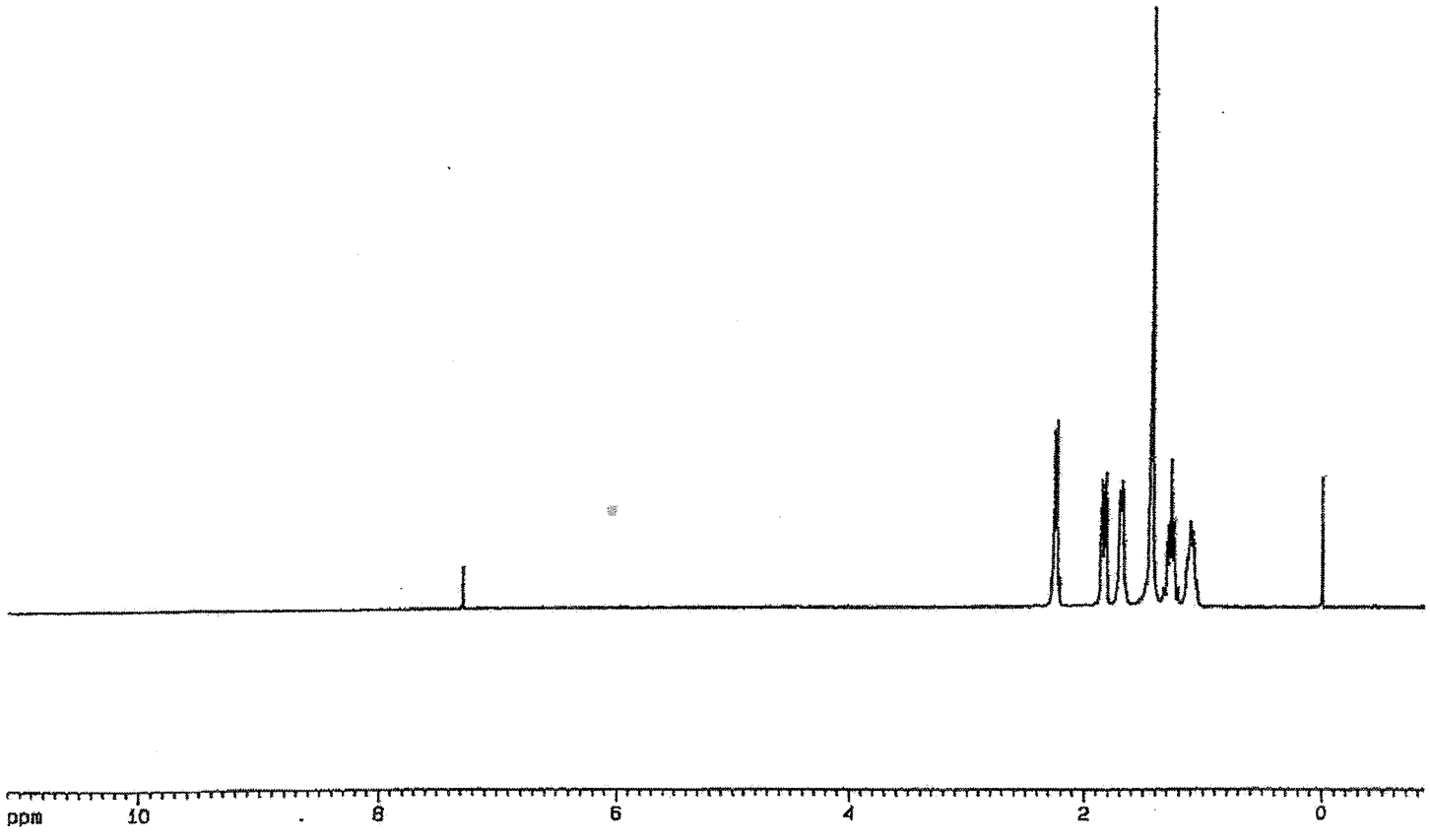
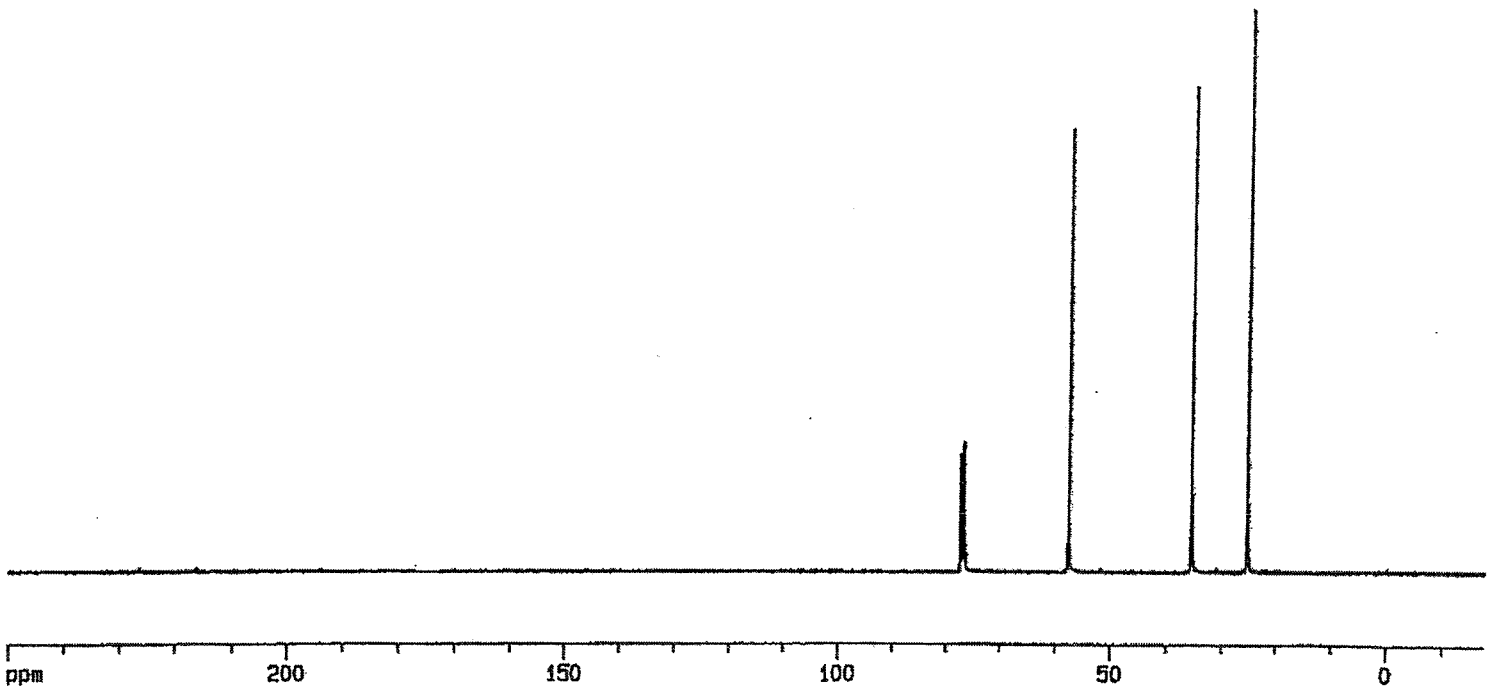
Wavenumbers (cm-1)



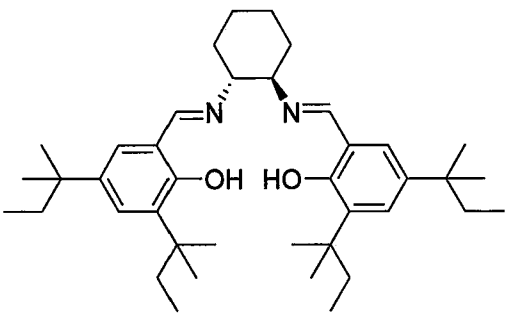
^{1}H NMR spectrum ($CDCl_3$/TMS) of (1R, 2R)-(-)-1, 2-diaminocyclohexane



^{13}C NMR spectrum ($CDCl_3$/TMS) of (1R, 2R)-(-)-1, 2-diaminocyclohexane

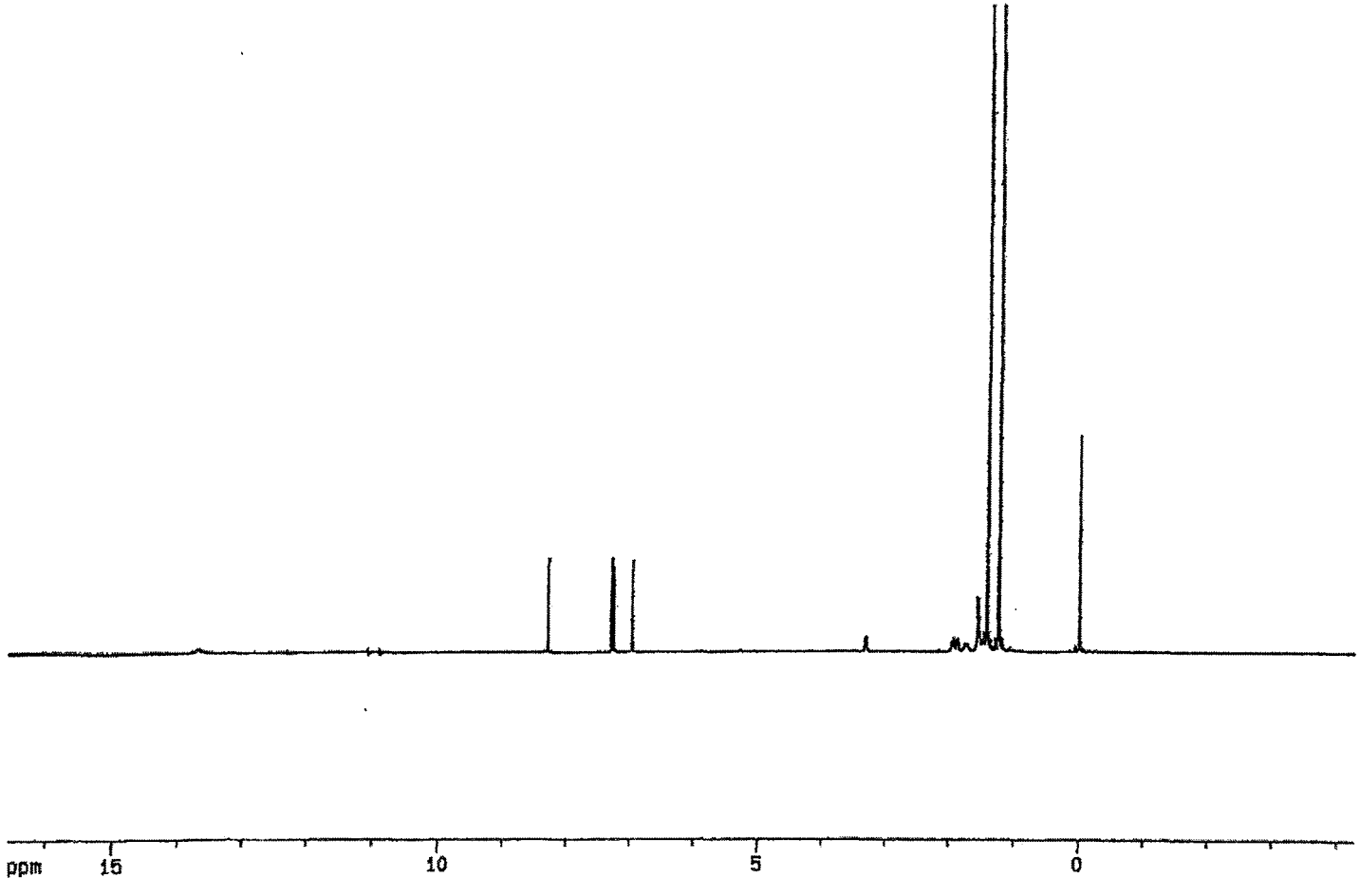
Appendix C

(R,R)-N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-cyclohexanediamine



(11)

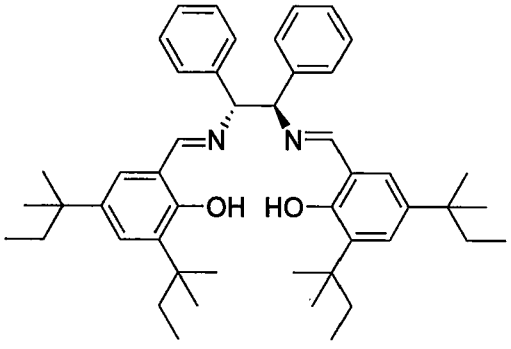
^{1}H NMR



^{1}H NMR spectrum ($CDCl_3$/TMS) of (R, R)-N, N'-bis(3, 5-*tert*-butylsalicylidene)-1, 2-cyclohexanediamine

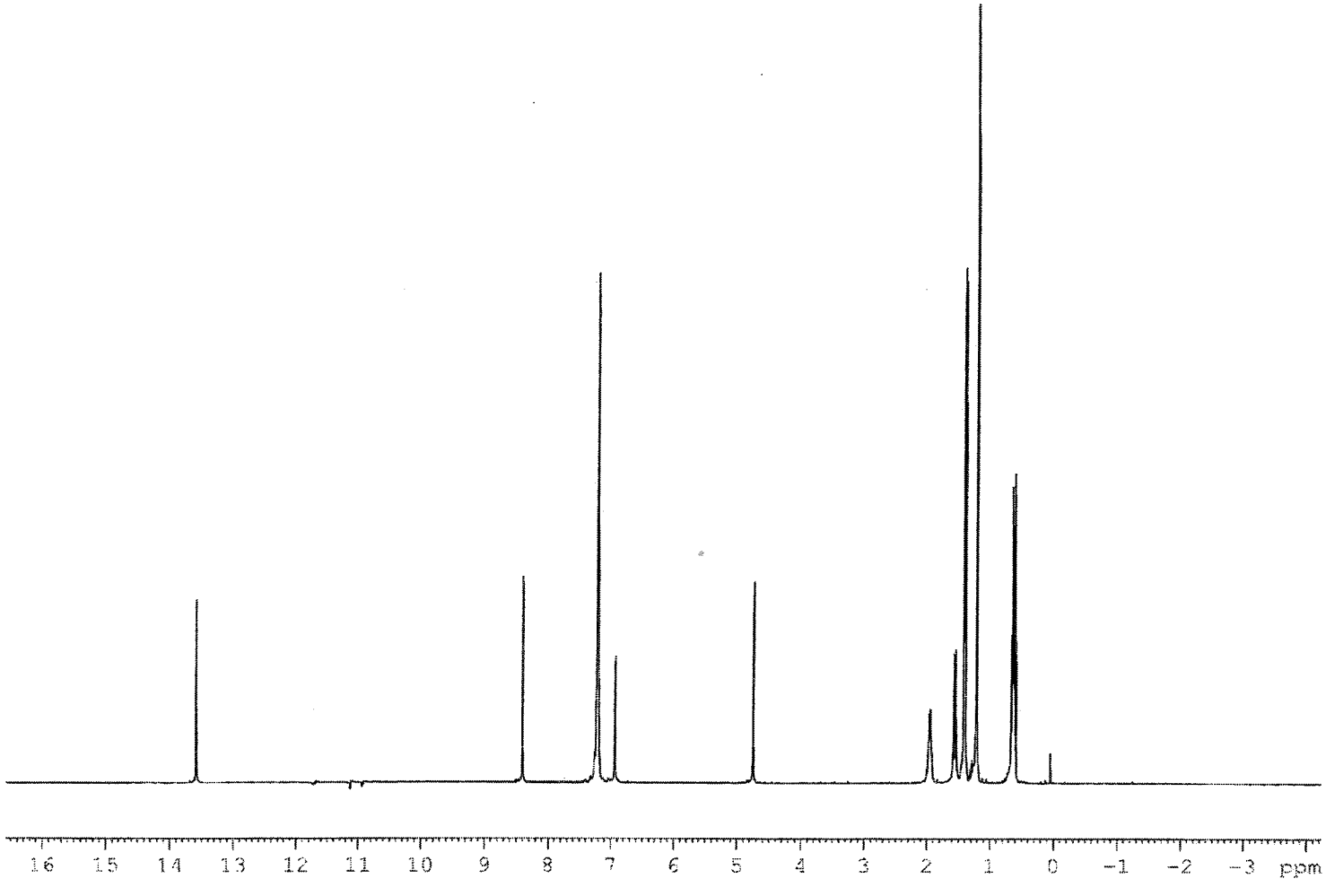
Appendix D

(R,R)-N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-diphenylethylenediamine



(12)

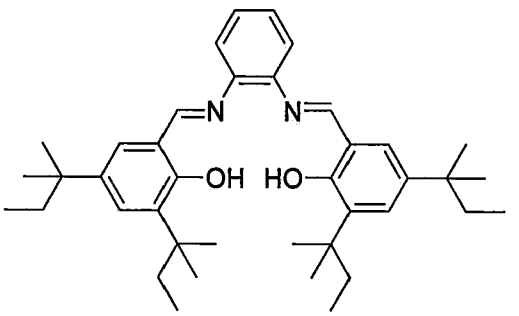
^{1}H NMR



Proton NMR for (R,R)–N,N'–Bis(3,5–di–t–pentylsalicylidene)–1,2–diphenylethylenediamine

Appendix E

N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-Phenylenediamine



(13)

Structure Determined from

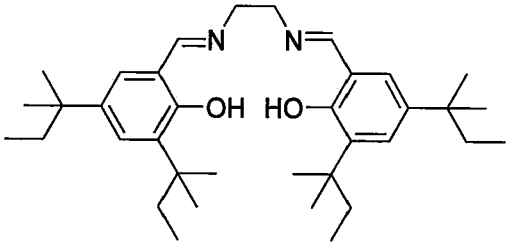
FT-IR, ^{1}H and ^{13}C NMR
data obtained from resulting transition

metal complexes

22-25

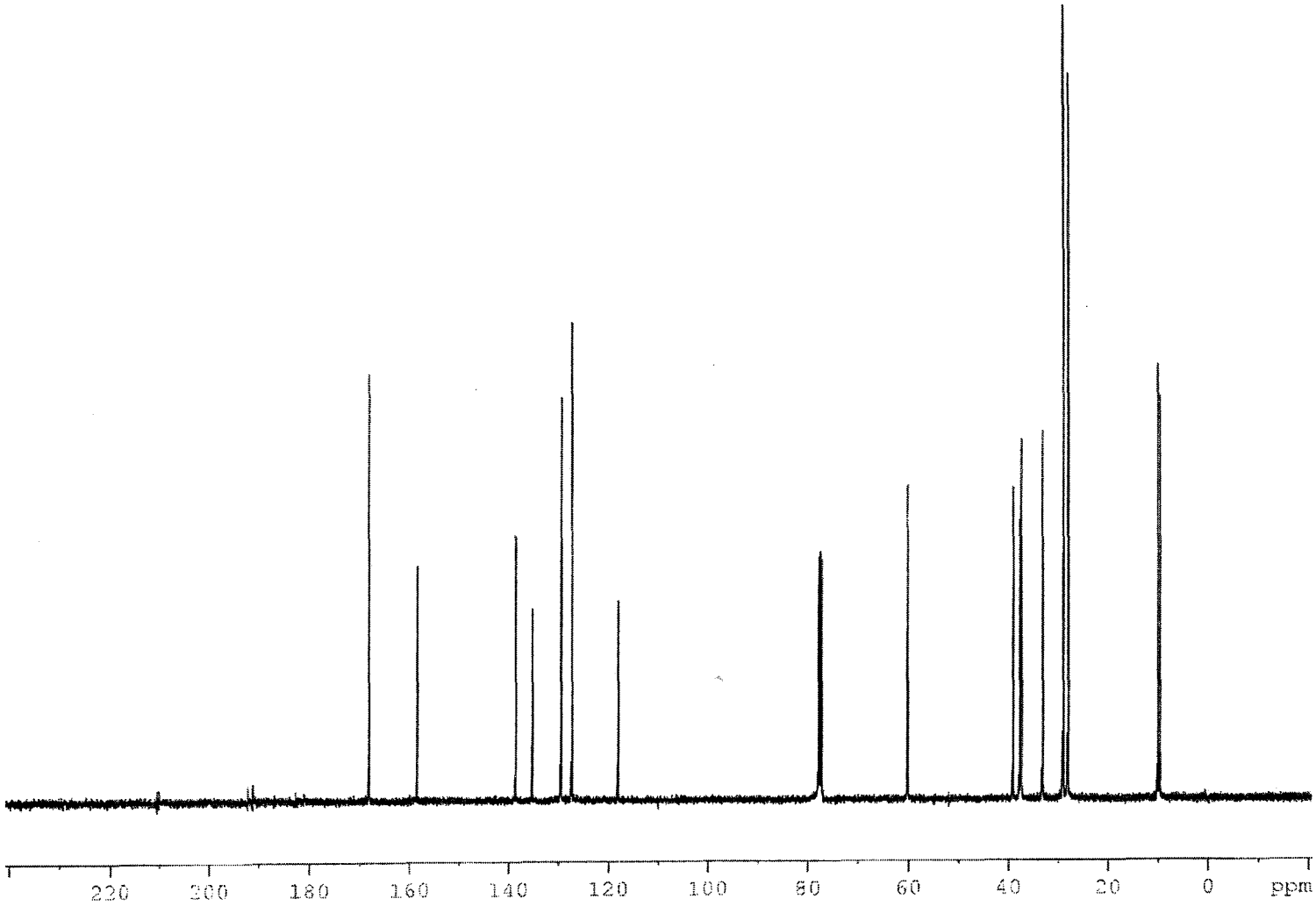
Appendix F

N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-ethylenediamine

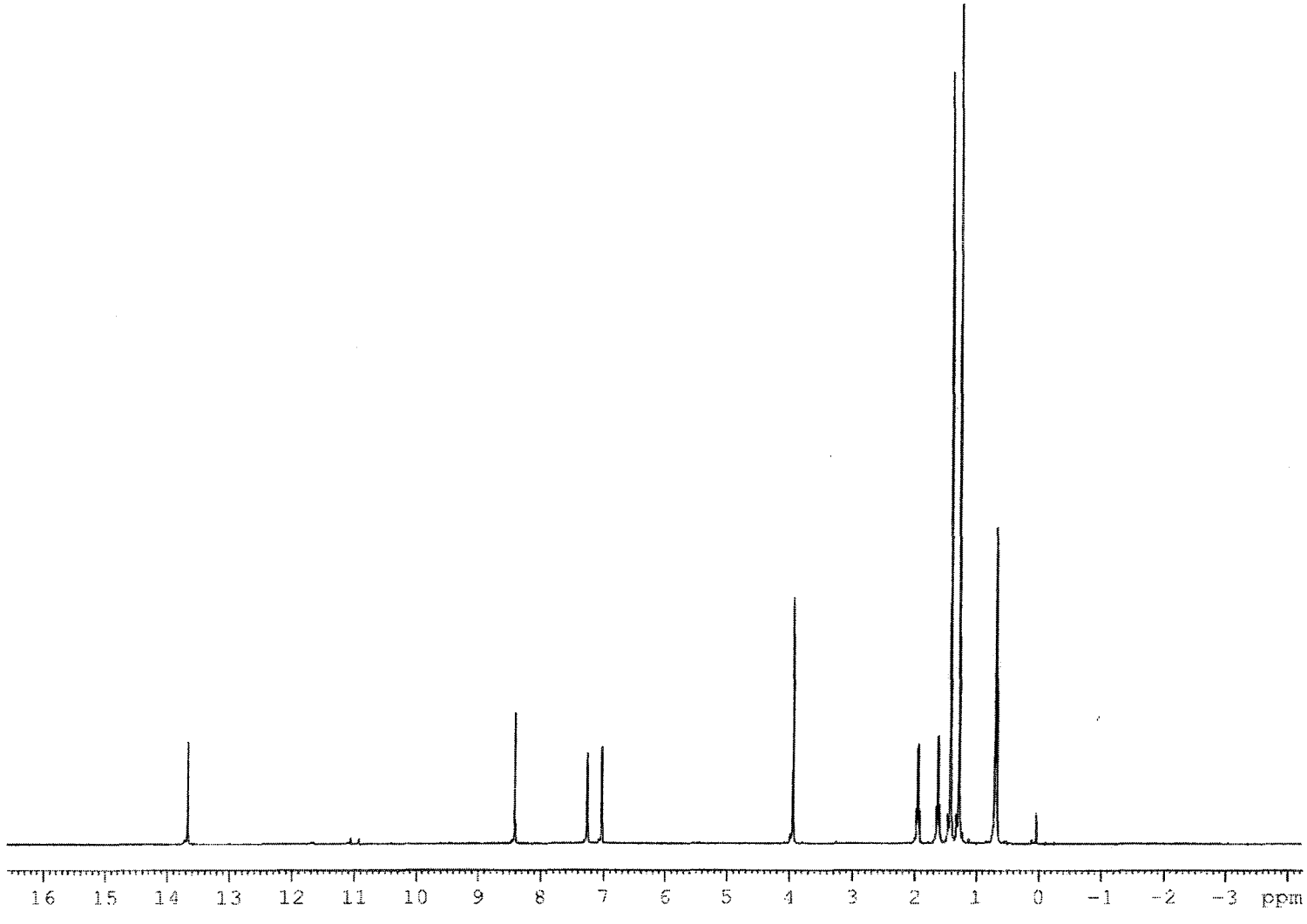


(14)

^{1}H NMR
^{13}C NMR
UV



Carbon 13 NMR for N,N'–Bis(3,5–di–t–pentylsalicylidene)–1,2–ethylenediamine



Proton NMR for N,N'-Bis(3,5-di-t-pentylsalicylidene)-1,2-ethylenediamine

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Time: 02:35

Wavelength Scan HELP

ReadSamples Tabulate +-*/Scans Scatter NetA Method SaveClear Print Quit

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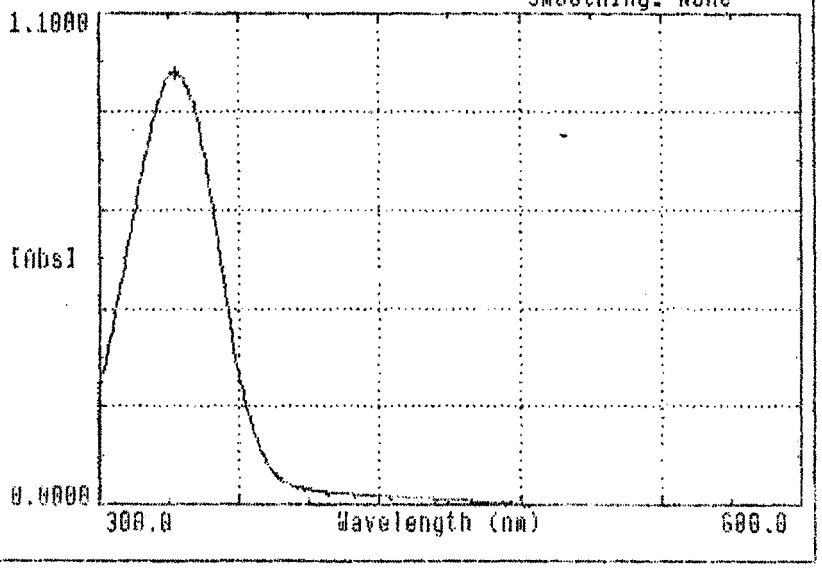
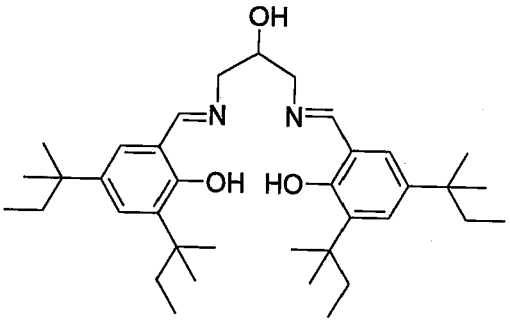


Appendix G

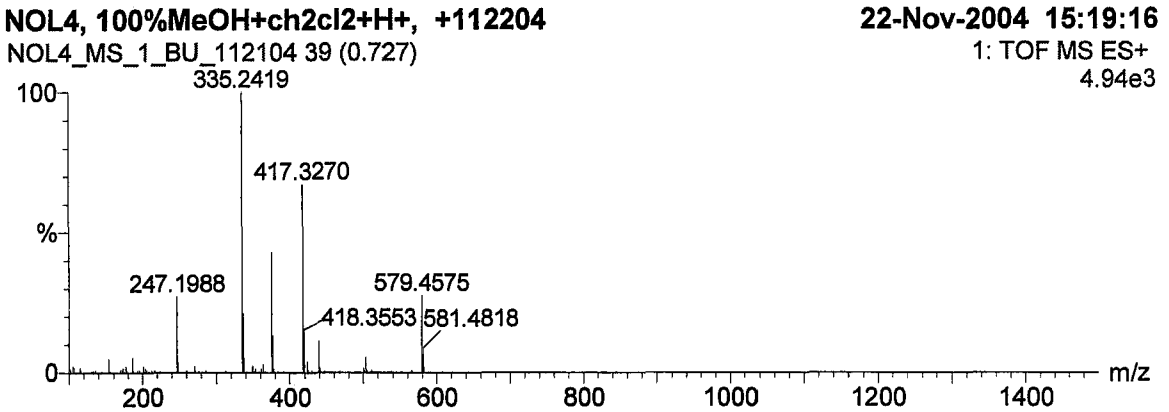
N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,3-diamino-propan-2-ol

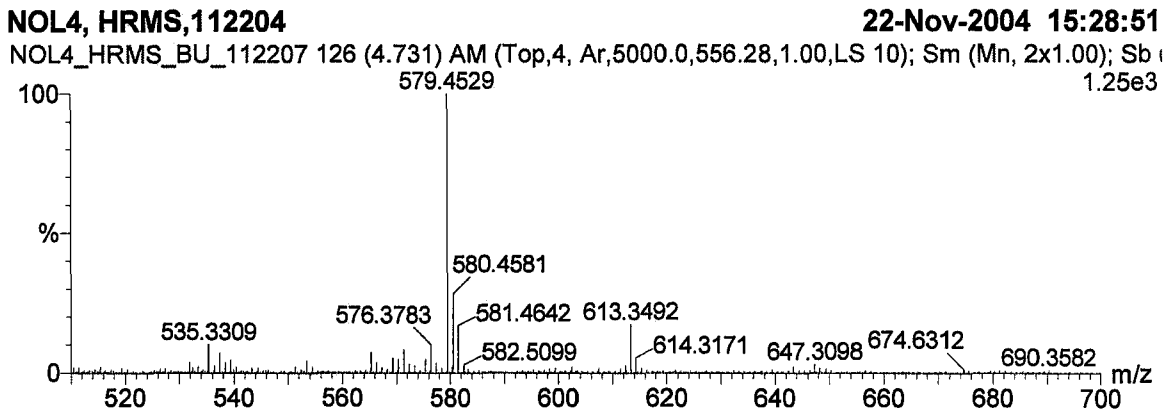


(15)

EI-MS

N,N'-Bis(3,5-di-t-pentylsalicylidene)-1,3-diamino-propan-2-ol





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Monoisotopic Mass, Even Electron Ions
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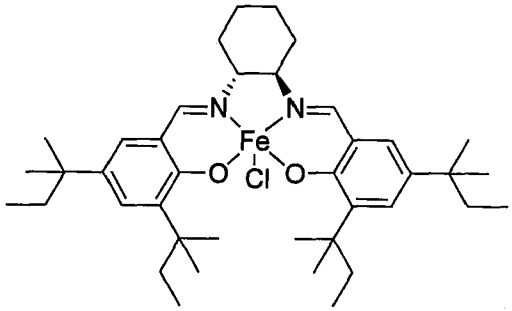
Formula					

Appendix H

(R,R)-N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-cyclohexanediamine ferric chloride



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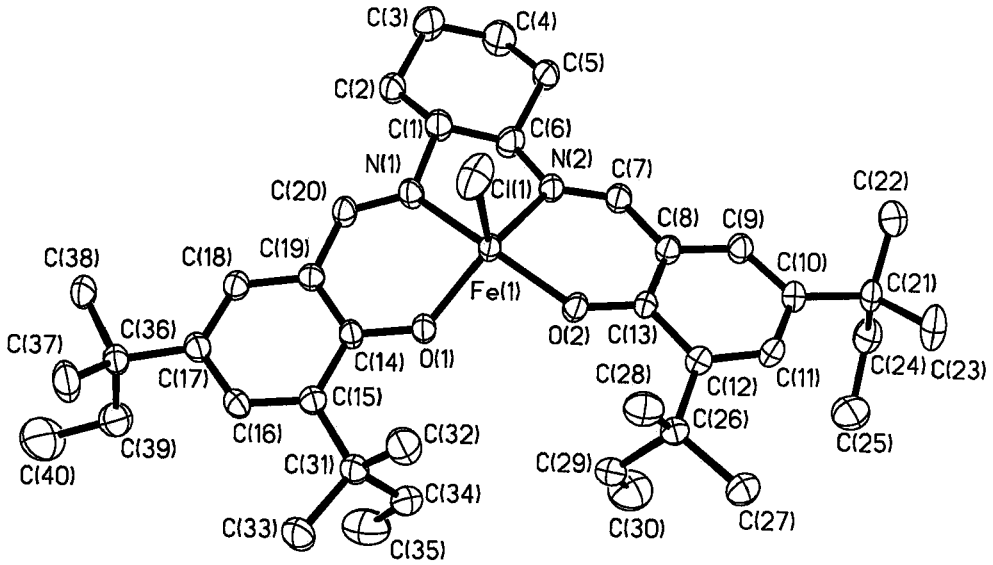
X-RAY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(R,R)-N,N'-Bis(3,5-di-t-pentylsalicylidene)-1,2-cyclohexanediamine ferric chloride

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_exptl_crystal_size_mid            0.19
_exptl_crystal_size_min            0.14
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_exptl_absorpt_coefficient_mu      0.497
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_diffrn_radiation_monochromator    graphite
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_diffrn_reflns_av_sigmaI/netI      0.0408
_diffrn_reflns_limit_h_min         -20
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_diffrn_reflns_limit_k_max         22
_diffrn_reflns_limit_l_min         -16
_diffrn_reflns_limit_l_max         16
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_computing_cell_refinement        ?
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_computing_structure_solution     'SHELXS-97 (Sheldrick, 1990)'
_computing_structure_refinement   'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics     ?
_computing_publication_material   ?

_refine_special_details
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR
and
 goodness of fit S are based on F^2^, conventional R-factors R are
based
 on F, with F set to zero for negative F^2^. The threshold expression
of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc.
and is
 not relevant to the choice of reflections for refinement.  R-factors
based
 on F^2^ are statistically about twice as large as those based on F,
and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0684P)^2^+3.7190P] where
P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     mixed
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          7835
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Fe1 Fe 0.13836(3) 0.65456(2) 0.11362(3) 0.02251(13) Uani 1 1 d . . .
Cl1 Cl 0.04431(6) 0.62268(5) 0.21173(7) 0.0470(2) Uani 1 1 d . . .
O2 O 0.19466(13) 0.73477(10) 0.18128(16) 0.0282(5) Uani 1 1 d . . .
O1 O 0.23471(13) 0.59598(10) 0.14209(17) 0.0289(5) Uani 1 1 d . . .
N2 N 0.07909(16) 0.72463(13) -0.0047(2) 0.0284(5) Uani 1 1 d . . .
N1 N 0.09535(16) 0.58628(13) -0.01363(19) 0.0285(6) Uani 1 1 d . . .
C1 C 0.0189(2) 0.61426(17) -0.0839(3) 0.0359(8) Uani 1 1 d . . .
H1 H -0.0251 0.6145 -0.0438 0.069(14) Uiso 1 1 calc R . .
C2 C -0.0138(2) 0.57331(17) -0.1850(3) 0.0352(7) Uani 1 1 d . . .
H2A H -0.0277 0.5255 -0.1681 0.047(8) Uiso 1 1 calc R . .
H2B H 0.0291 0.5709 -0.2268 0.047(8) Uiso 1 1 calc R . .
C3 C -0.0920(3) 0.61009(19) -0.2484(3) 0.0470(9) Uani 1 1 d . . .
H3A H -0.1081 0.5868 -0.3158 0.068(10) Uiso 1 1 calc R . .
H3B H -0.1376 0.6050 -0.2114 0.068(10) Uiso 1 1 calc R . .
C4 C -0.0781(3) 0.6872(2) -0.2660(3) 0.0527(10) Uani 1 1 d . . .
H4A H -0.1306 0.7084 -0.2992 0.087(12) Uiso 1 1 calc R . .
H4B H -0.0397 0.6919 -0.3136 0.087(12) Uiso 1 1 calc R . .
C5 C -0.0429(2) 0.72773(17) -0.1638(3) 0.0351(7) Uani 1 1 d . . .
H5A H -0.0305 0.7760 -0.1801 0.062(9) Uiso 1 1 calc R . .
H5B H -0.0838 0.7286 -0.1191 0.062(9) Uiso 1 1 calc R . .
C6 C 0.0369(2) 0.69101(17) -0.1068(3) 0.0360(8) Uani 1 1 d . . .
H6 H 0.0764 0.6912 -0.1534 0.069(14) Uiso 1 1 calc R . .
C7 C 0.08748(19) 0.79348(16) -0.0028(2) 0.0298(7) Uani 1 1 d . . .
H7 H 0.0584 0.8191 -0.0637 0.027(8) Uiso 1 1 calc R . .
C8 C 0.13607(18) 0.83532(15) 0.0814(2) 0.0259(6) Uani 1 1 d . . .
C9 C 0.13186(19) 0.91020(15) 0.0690(2) 0.0286(6) Uani 1 1 d . . .
H9 H 0.0966 0.9300 0.0071 0.045(10) Uiso 1 1 calc R . .
C10 C 0.17676(19) 0.95550(15) 0.1430(2) 0.0272(6) Uani 1 1 d . . .
C11 C 0.23094(19) 0.92317(16) 0.2286(2) 0.0281(6) Uani 1 1 d . . .
```

```
H11 H 0.2634 0.9540 0.2806 0.025(8) Uiso 1 1 calc R . .
C12 C 0.24137(18) 0.85034(15) 0.2443(2) 0.0257(6) Uani 1 1 d . . .
C13 C 0.19006(18) 0.80489(14) 0.1698(2) 0.0235(6) Uani 1 1 d . . .
C14 C 0.24857(18) 0.52786(15) 0.1240(2) 0.0251(6) Uani 1 1 d . . .
C15 C 0.31823(19) 0.49176(16) 0.1863(2) 0.0273(6) Uani 1 1 d . . .
C16 C 0.33106(19) 0.42142(16) 0.1606(2) 0.0298(7) Uani 1 1 d . . .
H16 H 0.3782 0.3969 0.2024 0.031(9) Uiso 1 1 calc R . .
C17 C 0.28045(19) 0.38331(16) 0.0782(2) 0.0279(6) Uani 1 1 d . . .
C18 C 0.21250(19) 0.41902(16) 0.0197(2) 0.0283(6) Uani 1 1 d . . .
H18 H 0.1762 0.3947 -0.0372 0.025(8) Uiso 1 1 calc R . .
C19 C 0.19499(18) 0.49056(15) 0.0416(2) 0.0254(6) Uani 1 1 d . . .
C20 C 0.12273(19) 0.52284(15) -0.0250(2) 0.0282(6) Uani 1 1 d . . .
H20 H 0.0925 0.4948 -0.0825 0.026(8) Uiso 1 1 calc R . .
C21 C 0.1740(2) 1.03696(15) 0.1270(2) 0.0294(6) Uani 1 1 d . . .
C22 C 0.0864(2) 1.06056(18) 0.0691(3) 0.0457(9) Uani 1 1 d . . .
H22A H 0.0744 1.0397 -0.0003 0.055(7) Uiso 1 1 calc R . .
H22B H 0.0850 1.1116 0.0630 0.055(7) Uiso 1 1 calc R . .
H22C H 0.0450 1.0452 0.1083 0.055(7) Uiso 1 1 calc R . .
C23 C 0.1922(3) 1.07722(18) 0.2327(3) 0.0471(9) Uani 1 1 d . . .
H23A H 0.1503 1.0651 0.2732 0.055(7) Uiso 1 1 calc R . .
H23B H 0.1906 1.1276 0.2195 0.055(7) Uiso 1 1 calc R . .
H23C H 0.2469 1.0641 0.2716 0.055(7) Uiso 1 1 calc R . .
C24 C 0.2370(2) 1.05904(18) 0.0576(3) 0.0393(8) Uani 1 1 d . . .
H24A H 0.2223 1.0346 -0.0090 0.043(7) Uiso 1 1 calc R . .
H24B H 0.2304 1.1092 0.0433 0.043(7) Uiso 1 1 calc R . .
C25 C 0.3292(2) 1.0445(2) 0.1033(4) 0.0527(10) Uani 1 1 d . . .
H25A H 0.3458 1.0703 0.1684 0.060(7) Uiso 1 1 calc R . .
H25B H 0.3629 1.0596 0.0538 0.060(7) Uiso 1 1 calc R . .
H25C H 0.3372 0.9944 0.1166 0.060(7) Uiso 1 1 calc R . .
C26 C 0.30804(19) 0.81932(16) 0.3345(2) 0.0286(6) Uani 1 1 d . . .
C27 C 0.3579(2) 0.87785(19) 0.4029(3) 0.0432(9) Uani 1 1 d . . .
H27A H 0.3862 0.9071 0.3596 0.044(6) Uiso 1 1 calc R . .
H27B H 0.3988 0.8564 0.4582 0.044(6) Uiso 1 1 calc R . .
H27C H 0.3201 0.9067 0.4337 0.044(6) Uiso 1 1 calc R . .
C28 C 0.2668(2) 0.77353(19) 0.4086(3) 0.0377(8) Uani 1 1 d . . .
H28A H 0.2314 0.8029 0.4424 0.057(7) Uiso 1 1 calc R . .
H28B H 0.3097 0.7521 0.4615 0.057(7) Uiso 1 1 calc R . .
H28C H 0.2335 0.7369 0.3685 0.057(7) Uiso 1 1 calc R . .
C29 C 0.37019(19) 0.77248(18) 0.2883(3) 0.0339(7) Uani 1 1 d . . .
H29A H 0.4128 0.7556 0.3457 0.041(7) Uiso 1 1 calc R . .
H29B H 0.3403 0.7316 0.2554 0.041(7) Uiso 1 1 calc R . .
C30 C 0.4131(3) 0.8082(3) 0.2085(4) 0.0595(11) Uani 1 1 d . . .
H30A H 0.3715 0.8234 0.1488 0.069(8) Uiso 1 1 calc R . .
H30B H 0.4510 0.7752 0.1854 0.069(8) Uiso 1 1 calc R . .
H30C H 0.4440 0.8489 0.2405 0.069(8) Uiso 1 1 calc R . .
C31 C 0.3794(2) 0.53038(17) 0.2749(3) 0.0318(7) Uani 1 1 d . . .
C32 C 0.3314(2) 0.56685(19) 0.3525(3) 0.0403(8) Uani 1 1 d . . .
H32A H 0.2953 0.6033 0.3159 0.041(6) Uiso 1 1 calc R . .
H32B H 0.3709 0.5879 0.4096 0.041(6) Uiso 1 1 calc R . .
```

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H32C H 0.2980 0.5321 0.3803 0.041(6) Uiso 1 1 calc R . .
C33 C 0.4419(2) 0.47829(19) 0.3413(3) 0.0454(9) Uani 1 1 d . . .
H33A H 0.4114 0.4429 0.3723 0.057(7) Uiso 1 1 calc R . .
H33B H 0.4784 0.5040 0.3965 0.057(7) Uiso 1 1 calc R . .
H33C H 0.4749 0.4554 0.2967 0.057(7) Uiso 1 1 calc R . .
C34 C 0.4292(2) 0.58679(18) 0.2254(3) 0.0392(8) Uani 1 1 d . . .
H34A H 0.3901 0.6201 0.1862 0.050(8) Uiso 1 1 calc R . .
H34B H 0.4646 0.6126 0.2815 0.050(8) Uiso 1 1 calc R . .
C35 C 0.4840(3) 0.5566(3) 0.1521(4) 0.0632(12) Uani 1 1 d . . .
H35A H 0.5267 0.5264 0.1919 0.090(10) Uiso 1 1 calc R . .
H35B H 0.5101 0.5950 0.1213 0.090(10) Uiso 1 1 calc R . .
H35C H 0.4496 0.5293 0.0969 0.090(10) Uiso 1 1 calc R . .
C36 C 0.3037(2) 0.30599(16) 0.0561(3) 0.0310(7) Uani 1 1 d . . .
C37 C 0.3112(3) 0.26173(18) 0.1586(3) 0.0464(9) Uani 1 1 d . . .
H37A H 0.2595 0.2647 0.1840 0.049(6) Uiso 1 1 calc R . .
H37B H 0.3565 0.2800 0.2113 0.049(6) Uiso 1 1 calc R . .
H37C H 0.3223 0.2129 0.1440 0.049(6) Uiso 1 1 calc R . .
C38 C 0.2366(2) 0.27184(17) -0.0292(3) 0.0392(8) Uani 1 1 d . . .
H38A H 0.2523 0.2235 -0.0405 0.054(7) Uiso 1 1 calc R . .
H38B H 0.2319 0.2982 -0.0940 0.054(7) Uiso 1 1 calc R . .
H38C H 0.1835 0.2723 -0.0069 0.054(7) Uiso 1 1 calc R . .
C39 C 0.3882(2) 0.3076(2) 0.0177(3) 0.0471(9) Uani 1 1 d . . .
H39A H 0.3814 0.3370 -0.0445 0.032(6) Uiso 1 1 calc R . .
H39B H 0.4296 0.3300 0.0714 0.032(6) Uiso 1 1 calc R . .
C40 C 0.4221(3) 0.2358(3) -0.0081(4) 0.0760(15) Uani 1 1 d . . .
H40A H 0.4281 0.2053 0.0527 0.161(19) Uiso 1 1 calc R . .
H40B H 0.4759 0.2421 -0.0274 0.161(19) Uiso 1 1 calc R . .
H40C H 0.3837 0.2145 -0.0661 0.161(19) Uiso 1 1 calc R . .

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Cl1 0.0620(6) 0.0404(5) 0.0465(5) -0.0112(4) 0.0302(4) -0.0171(4)
O2 0.0329(11) 0.0182(10) 0.0294(11) 0.0002(8) -0.0038(9) -0.0024(8)
O1 0.0325(11) 0.0200(10) 0.0307(11) -0.0031(8) -0.0027(9) 0.0028(8)
N2 0.0299(13) 0.0211(12) 0.0302(13) -0.0011(10) -0.0038(11) 0.0012(10)
N1 0.0342(14) 0.0234(13) 0.0241(13) -0.0016(10) -0.0033(11) 0.0048(10)
C1 0.0386(18) 0.0277(17) 0.0343(18) -0.0028(13) -0.0100(15) 0.0042(14)
C2 0.0376(17) 0.0260(16) 0.0367(17) -0.0052(13) -0.0053(14) 0.0026(13)
C3 0.051(2) 0.039(2) 0.040(2) -0.0080(16) -0.0179(17) -0.0013(17)
C4 0.056(2) 0.043(2) 0.047(2) 0.0039(17) -0.0209(19) 0.0049(18)
C5 0.0358(17) 0.0248(15) 0.0385(18) 0.0034(13) -0.0082(14) 0.0018(13)
C6 0.0398(18) 0.0301(17) 0.0316(17) -0.0022(13) -0.0091(14) -0.0019(14)
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C7 0.0333(16) 0.0240(15) 0.0280(15) -0.0001(12) -0.0042(13) 0.0022(12)
C8 0.0299(15) 0.0219(14) 0.0250(14) -0.0023(11) 0.0035(12) -0.0009(12)
C9 0.0347(16) 0.0209(14) 0.0275(15) 0.0002(12) -0.0007(13) 0.0015(12)
C10 0.0325(16) 0.0197(14) 0.0298(15) -0.0024(11) 0.0071(13) 0.0003(12)
C11 0.0296(15) 0.0230(14) 0.0305(15) -0.0063(12) 0.0034(12) -0.0052(12)
C12 0.0270(14) 0.0240(14) 0.0257(14) -0.0019(12) 0.0046(12) -0.0017(12)
C13 0.0250(14) 0.0183(13) 0.0259(14) -0.0035(11) 0.0021(11) -0.0004(11)
C14 0.0290(14) 0.0187(13) 0.0274(15) 0.0008(11) 0.0046(12) 0.0023(11)
C15 0.0282(15) 0.0249(15) 0.0270(15) -0.0011(12) 0.0007(12) 0.0006(12)
C16 0.0305(16) 0.0239(15) 0.0319(16) 0.0030(12) -0.0008(13) 0.0054(12)
C17 0.0306(15) 0.0229(15) 0.0294(15) 0.0011(12) 0.0040(12) 0.0026(12)
C18 0.0317(15) 0.0231(14) 0.0287(15) -0.0021(12) 0.0024(13) -0.0005(12)
C19 0.0268(14) 0.0243(14) 0.0238(14) 0.0000(11) 0.0022(12) 0.0007(12)
C20 0.0361(16) 0.0212(14) 0.0247(14) -0.0029(11) 0.0001(12) 0.0013(12)
C21 0.0383(17) 0.0172(14) 0.0325(16) -0.0038(12) 0.0064(13) 0.0001(12)
C22 0.046(2) 0.0252(17) 0.063(2) 0.0003(16) 0.0046(18) 0.0034(15)
C23 0.074(3) 0.0233(16) 0.044(2) -0.0080(15) 0.0124(19) -0.0004(17)
C24 0.049(2) 0.0289(17) 0.0398(19) 0.0001(14) 0.0085(16) -0.0036(15)
C25 0.039(2) 0.048(2) 0.073(3) 0.002(2) 0.0154(19) -0.0084(17)
C26 0.0268(15) 0.0268(15) 0.0290(15) -0.0032(12) -0.0021(12) 0.0015(12)
C27 0.0429(19) 0.0371(19) 0.042(2) -0.0095(16) -0.0113(16) 0.0020(16)
C28 0.0382(18) 0.046(2) 0.0263(16) 0.0034(14) 0.0011(14) 0.0015(15)
C29 0.0261(15) 0.0343(17) 0.0389(18) -0.0041(14) 0.0004(13) 0.0030(13)
C30 0.048(2) 0.073(3) 0.062(3) -0.003(2) 0.024(2) -0.003(2)
C31 0.0331(16) 0.0268(15) 0.0309(16) -0.0018(13) -0.0044(13) 0.0039(13)
C32 0.047(2) 0.0404(19) 0.0296(17) -0.0046(14) -0.0013(15) 0.0072(16)
C33 0.047(2) 0.0349(19) 0.044(2) -0.0039(16) -0.0155(16) 0.0098(16)
C34 0.0336(17) 0.0341(18) 0.045(2) 0.0009(15) -0.0043(15) -0.0025(14)
C35 0.044(2) 0.080(3) 0.065(3) 0.010(2) 0.009(2) 0.000(2)
C36 0.0347(16) 0.0216(15) 0.0341(17) -0.0011(12) 0.0006(13) 0.0028(12)
C37 0.063(2) 0.0248(17) 0.046(2) 0.0026(15) -0.0012(18) 0.0063(16)
C38 0.0443(19) 0.0225(16) 0.046(2) -0.0064(14) -0.0034(16) 0.0015(14)
C39 0.0397(19) 0.040(2) 0.061(2) -0.0152(18) 0.0093(18) 0.0035(16)
C40 0.063(3) 0.074(3) 0.091(4) -0.029(3) 0.015(3) 0.015(3)

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 All esds (except the esd in the dihedral angle between two l.s.
planes)
 are estimated using the full covariance matrix.  The cell esds are
taken
 into account individually in the estimation of esds in distances,
angles
 and torsion angles; correlations between esds in cell parameters are
only
 used when they are defined by crystal symmetry.  An approximate
(isotropic)
 treatment of cell esds is used for estimating esds involving l.s.
planes.
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Fe1 O1 1.885(2) . ?
Fe1 N1 2.089(2) . ?
Fe1 N2 2.096(3) . ?
Fe1 Cl1 2.2436(11) . ?
O2 C13 1.324(3) . ?
O1 C14 1.326(3) . ?
N2 C7 1.299(4) . ?
N2 C6 1.496(4) . ?
N1 C20 1.288(4) . ?
N1 C1 1.478(4) . ?
C1 C6 1.510(5) . ?
C1 C2 1.515(4) . ?
C2 C3 1.530(5) . ?
C3 C4 1.488(5) . ?
C4 C5 1.530(5) . ?
C5 C6 1.520(4) . ?
C7 C8 1.440(4) . ?
C8 C13 1.413(4) . ?
C8 C9 1.414(4) . ?
C9 C10 1.373(4) . ?
C10 C11 1.405(4) . ?
C10 C21 1.541(4) . ?
C11 C12 1.386(4) . ?
C12 C13 1.422(4) . ?
C12 C26 1.536(4) . ?
C14 C19 1.416(4) . ?
C14 C15 1.421(4) . ?
C15 C16 1.386(4) . ?
C15 C31 1.537(4) . ?
C16 C17 1.403(4) . ?
C17 C18 1.379(4) . ?
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C18 C19 1.412(4) . ?
C19 C20 1.441(4) . ?
C21 C22 1.532(5) . ?
C21 C23 1.534(4) . ?
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C26 C27 1.534(4) . ?
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C31 C33 1.540(4) . ?
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O1 Fe1 N2 138.59(10) . . ?
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N1 C1 C2 117.1(3) . . ?
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C4 C3 C2 112.6(3) . . ?
C3 C4 C5 113.2(3) . . ?
C6 C5 C4 109.1(3) . . ?
N2 C6 C1 107.6(3) . . ?
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C1 C6 C5 110.4(3) . . ?
N2 C7 C8 126.6(3) . . ?
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O2 C13 C8 120.2(2) . . ?
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C8 C13 C12 119.2(3) . . ?
O1 C14 C19 120.5(3) . . ?
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C19 C14 C15 119.3(3) . . ?
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C16 C15 C31 121.4(3) . . ?
C14 C15 C31 121.3(3) . . ?
C15 C16 C17 125.0(3) . . ?
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C18 C17 C36 123.7(3) . . ?
C16 C17 C36 119.5(3) . . ?
C17 C18 C19 121.5(3) . . ?
C18 C19 C14 120.1(3) . . ?
C18 C19 C20 116.9(3) . . ?
C14 C19 C20 123.0(3) . . ?
N1 C20 C19 125.3(3) . . ?
C22 C21 C23 106.7(3) . . ?
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C23 C21 C24 110.5(3) . . ?
C22 C21 C10 110.6(3) . . ?
C23 C21 C10 111.9(3) . . ?
C24 C21 C10 109.8(2) . . ?
C25 C24 C21 116.1(3) . . ?
C28 C26 C27 106.8(3) . . ?
C28 C26 C12 110.9(2) . . ?
C27 C26 C12 112.0(3) . . ?
C28 C26 C29 108.6(3) . . ?
C27 C26 C29 108.6(3) . . ?
C12 C26 C29 109.8(2) . . ?
C30 C29 C26 115.7(3) . . ?
C15 C31 C33 111.7(3) . . ?
C15 C31 C32 110.9(3) . . ?
C33 C31 C32 106.4(3) . . ?
C15 C31 C34 109.3(3) . . ?
C33 C31 C34 108.9(3) . . ?
C32 C31 C34 109.6(3) . . ?
```

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C38 C36 C37 108.4(3) . . ?
C17 C36 C37 109.3(3) . . ?
C38 C36 C39 109.1(3) . . ?
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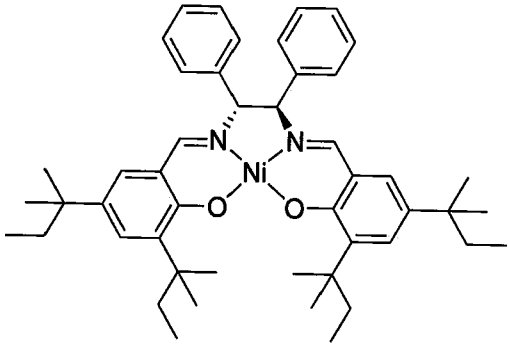
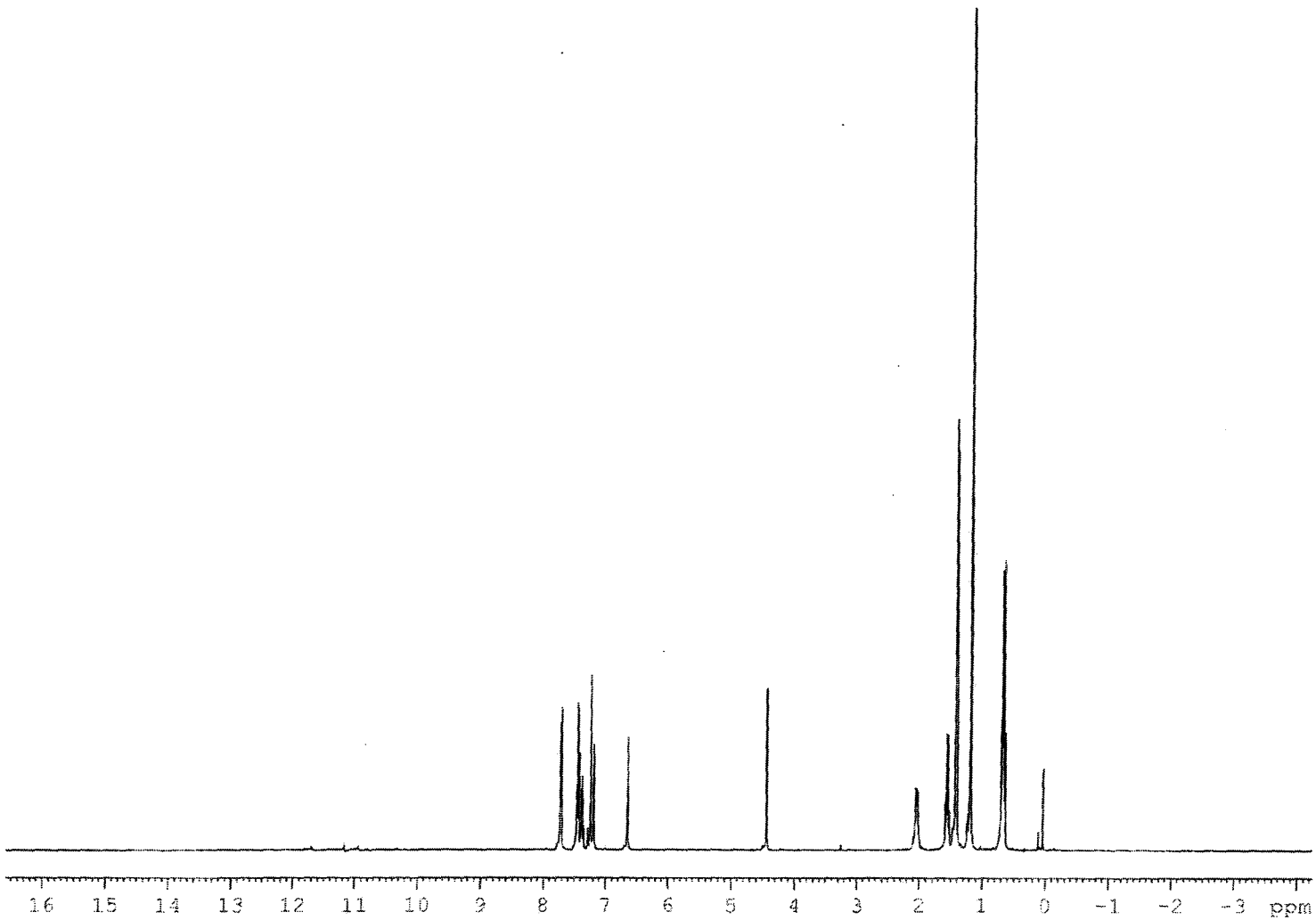
Appendix I

(R,R)-N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-diphenylethylenediamine nickel (II) complex

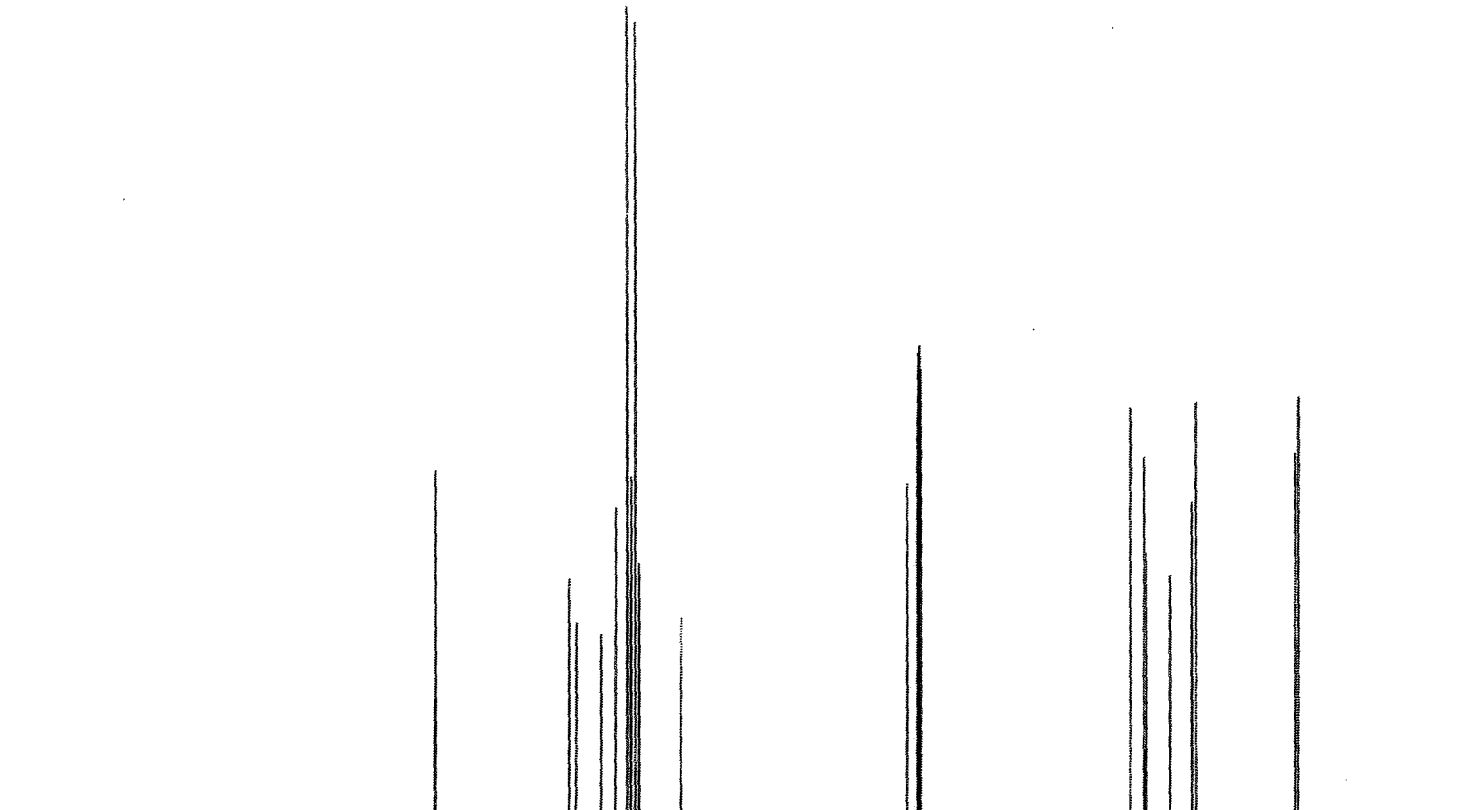


(17)

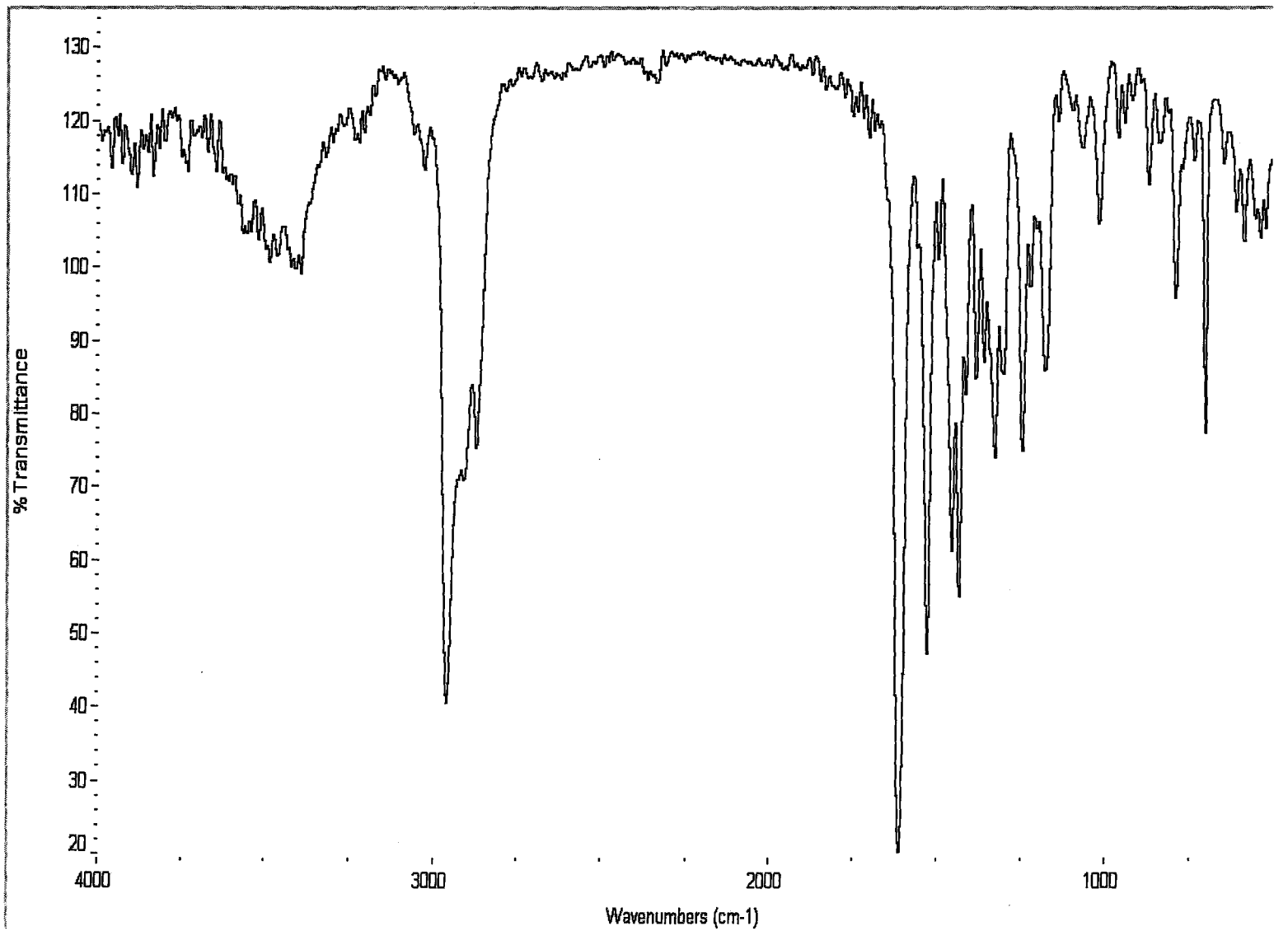
^{1}H NMR
^{13}C NMR
FT-IR



Proton NMR for (R,R)–N,N'–Bis(3,5–di–t–pentylsalicylidene)–1,2–diphenylethylenediamine nickel (II) complex

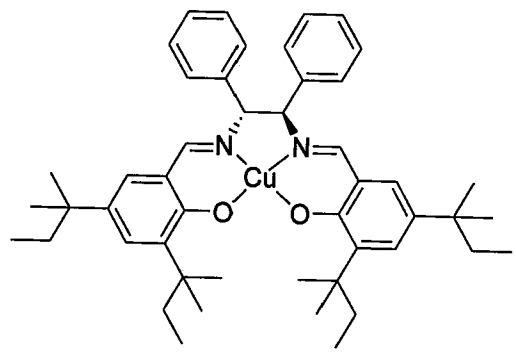


Carbon 13 NMR for (R,R)–N,N'–Bis(3,5–di–t–pentylsalicylidene)–1,2–diphenylethylenediamine nickel (II) complex


130
120
110
100
90
80
70
60
50
40
30
20
% Transmittance
4000
3000
2000
1000
Wavenumbers (cm-1)

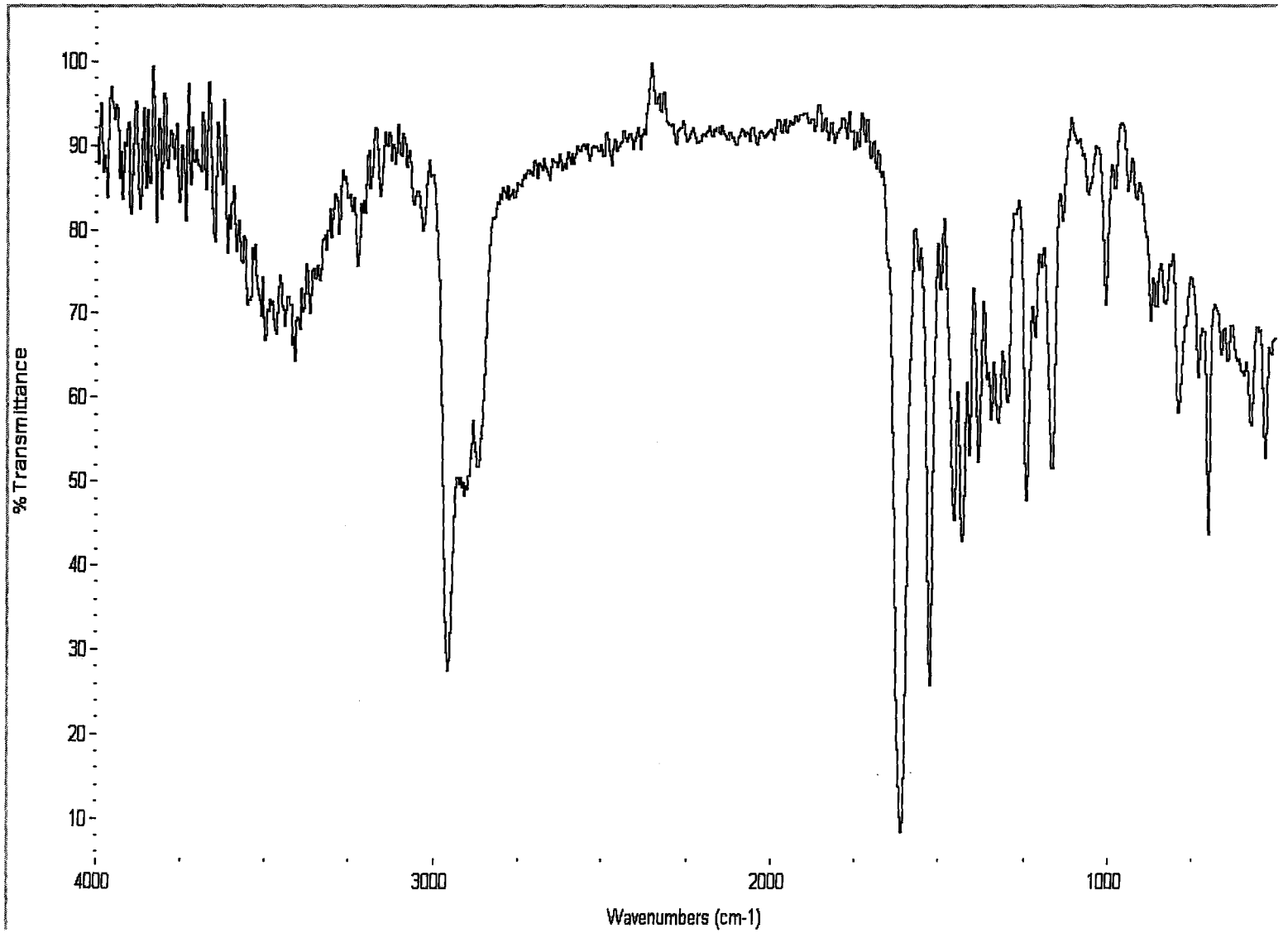
Appendix J

(R,R)-N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-diphenylethylenediamine copper (II) complex



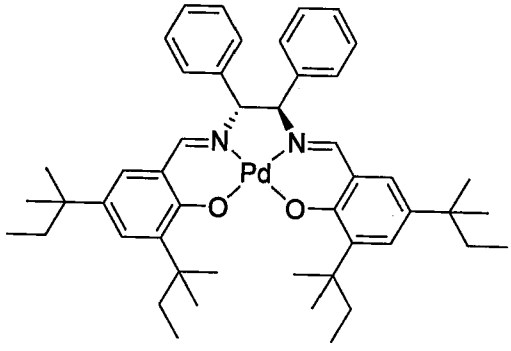
(18)

FT-IR


100
90
80
70
60
50
40
30
20
10
% Transmittance
4000
3000
2000
1000
Wavenumbers (cm-1)

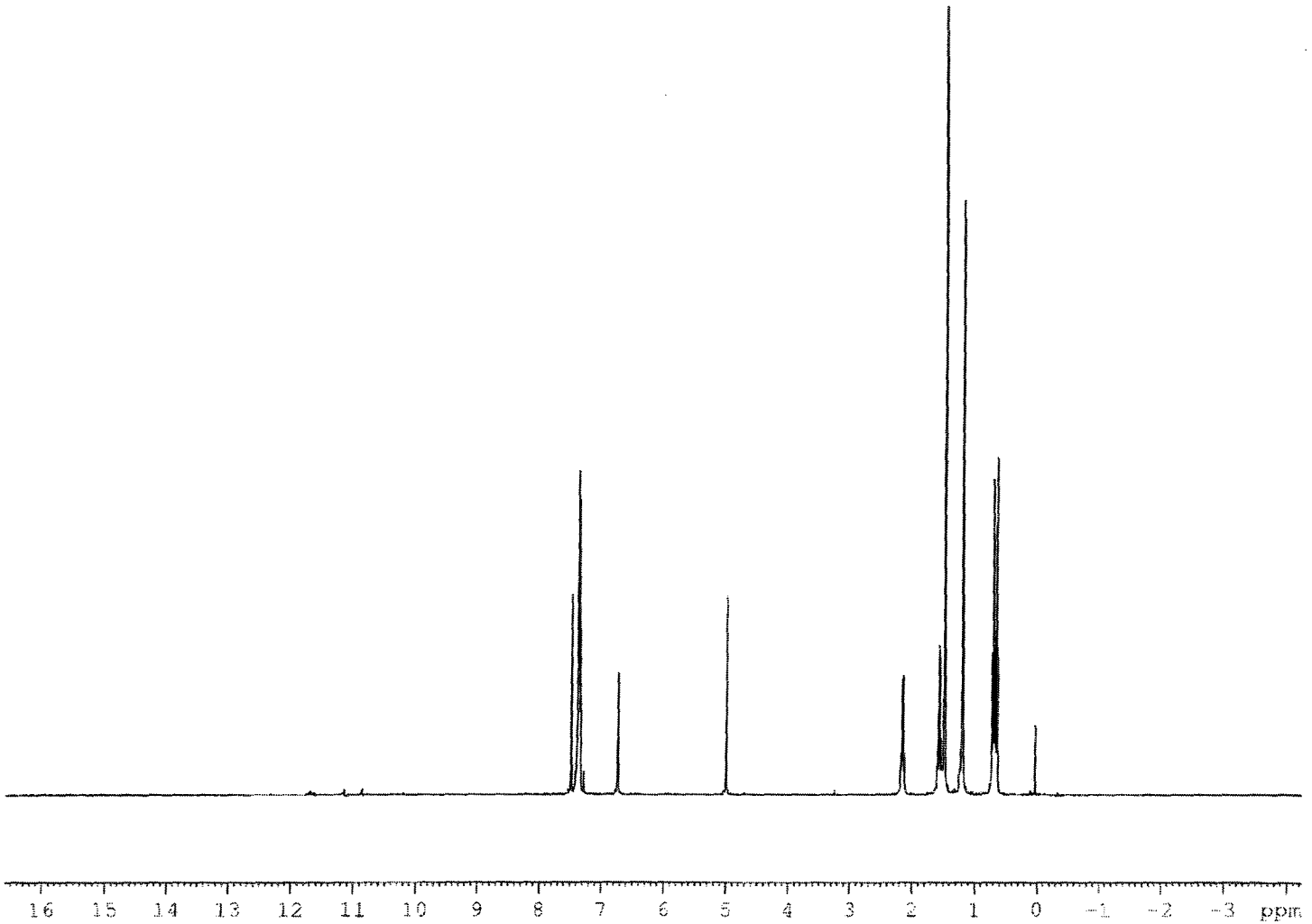
Appendix K

(R,R)-N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-diphenylethylenediamine palladium (II) complex

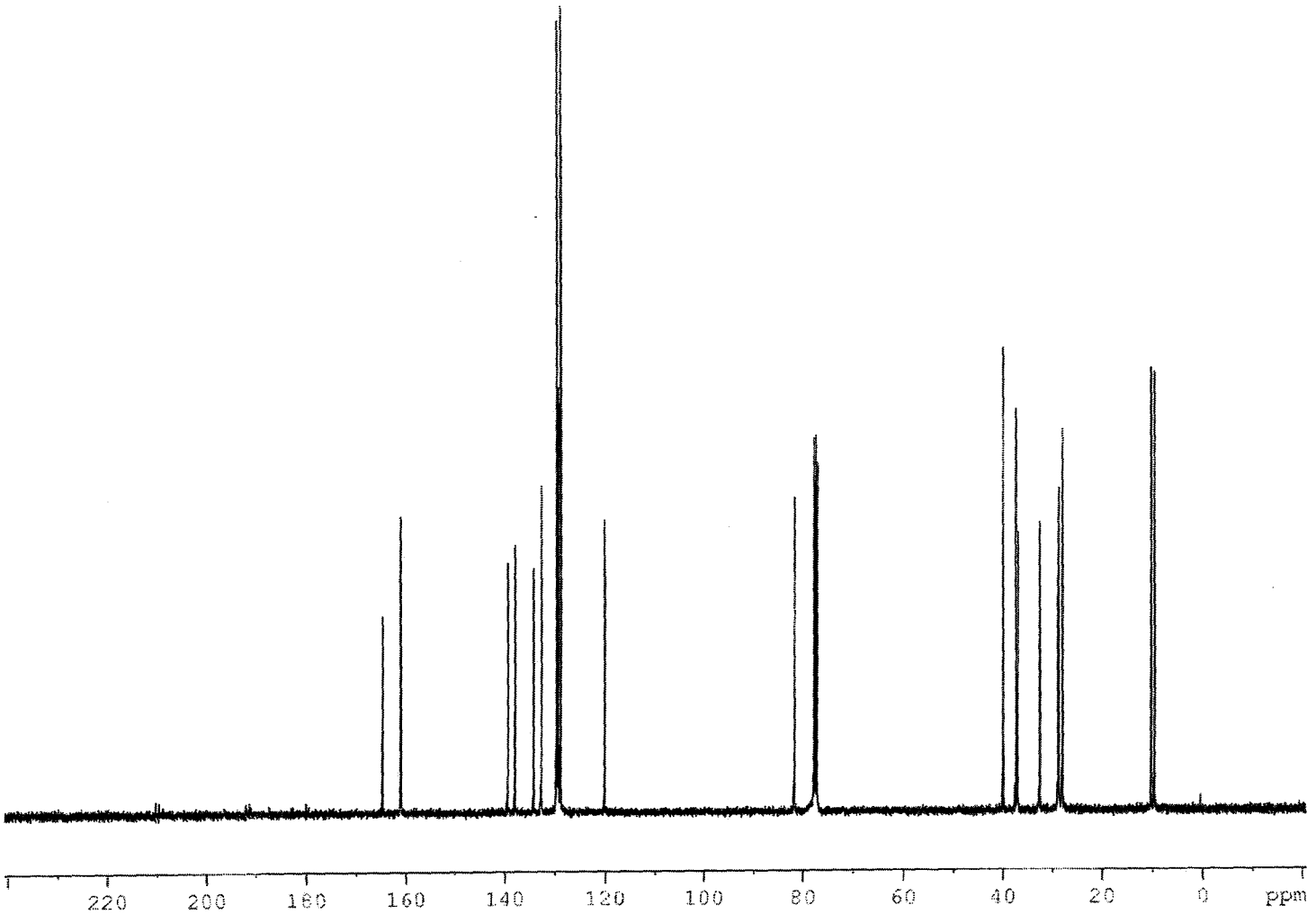


(19)

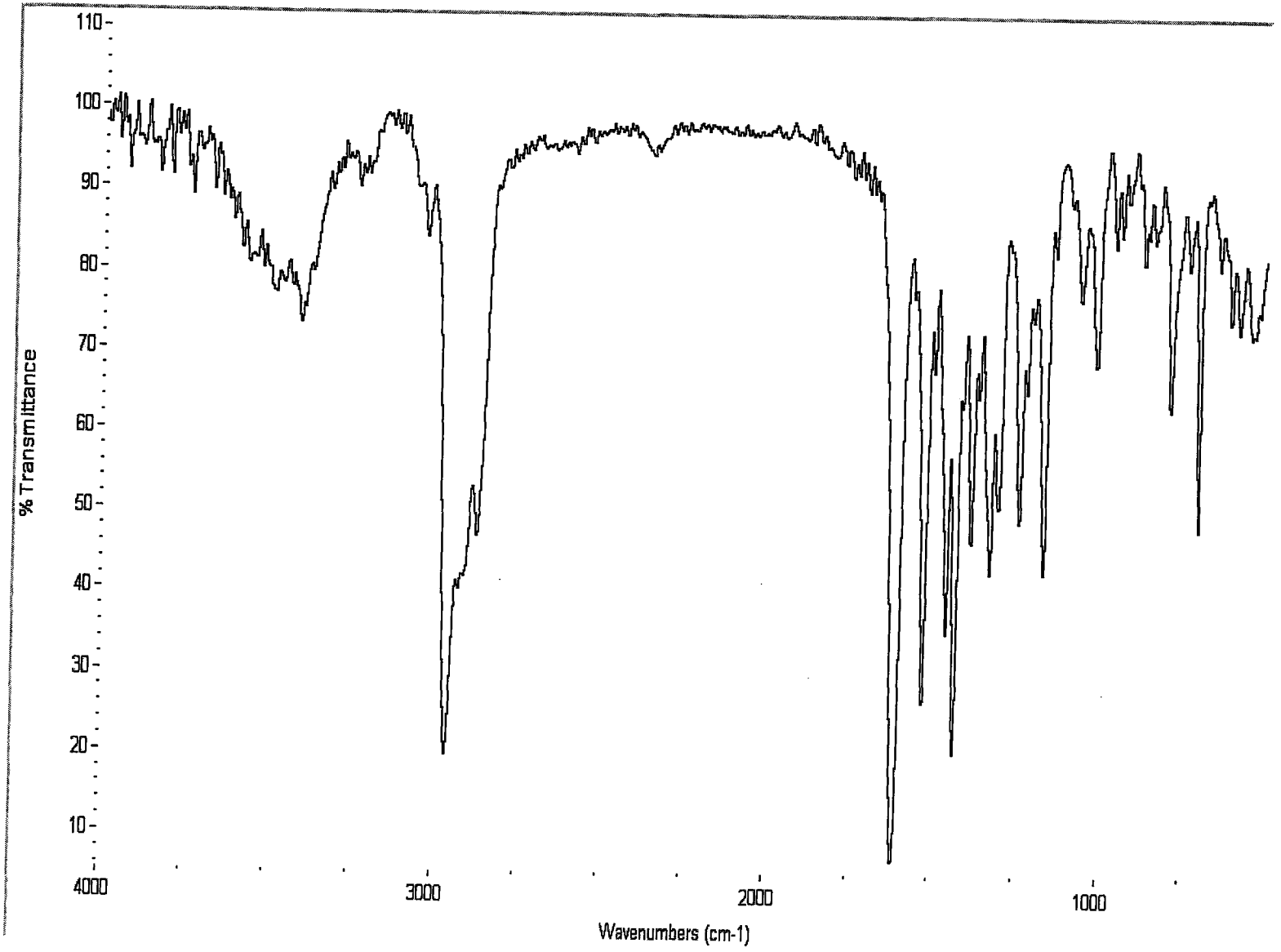
^{1}H NMR
^{13}C NMR
FT-IR



Proton NMR for (R,R)–N,N'–Bis(3,5–di–t–pentylsalicylidene)–1,2–diphenylethylenediamine palladium (II) complex

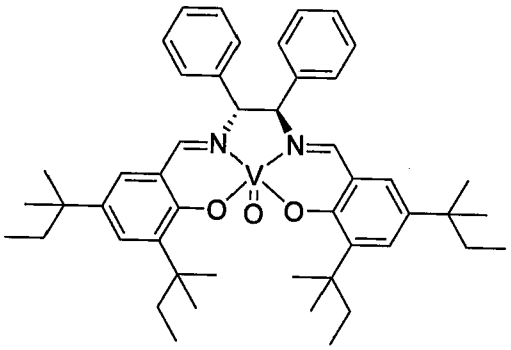


Carbon 13 NMR for (R,R)–N,N'–Bis(3,5–di–t–pentylsalicylidene)–1,2–diphenylethylenediamine palladium (II) complex


110
100
90
80
70
60
50
40
30
20
10
% Transmittance
4000
3000
2000
1000
Wavenumbers (cm-1)

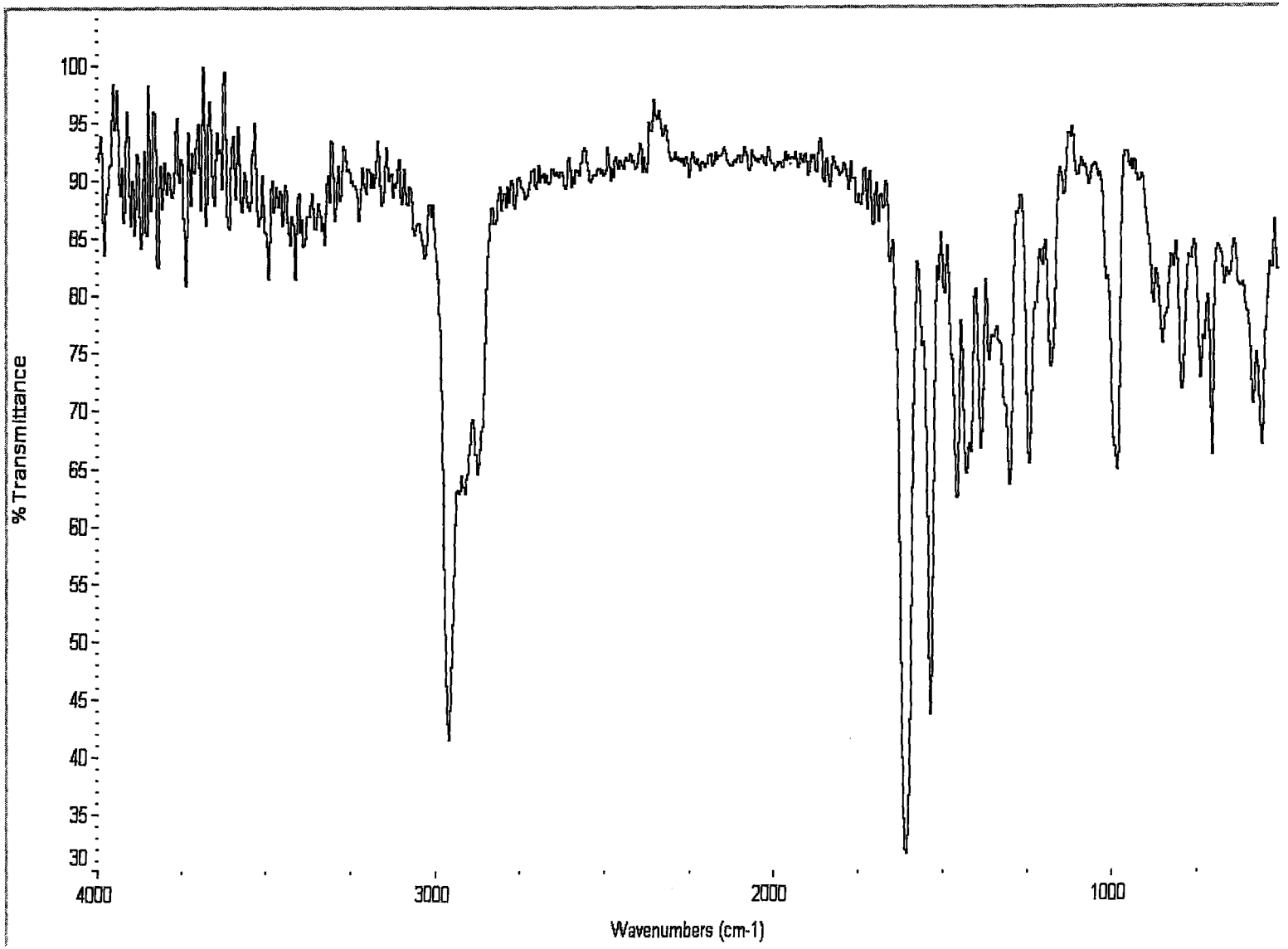
Appendix L

(R,R)-N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-diphenylethylenediamine vanadyl (II) complex



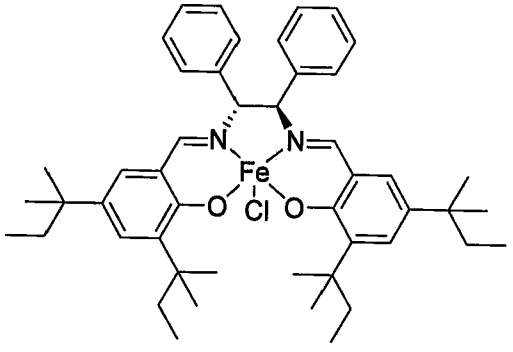
(20)

FT-IR


% Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
4000
3000
2000
1000
Wavenumbers (cm-1)

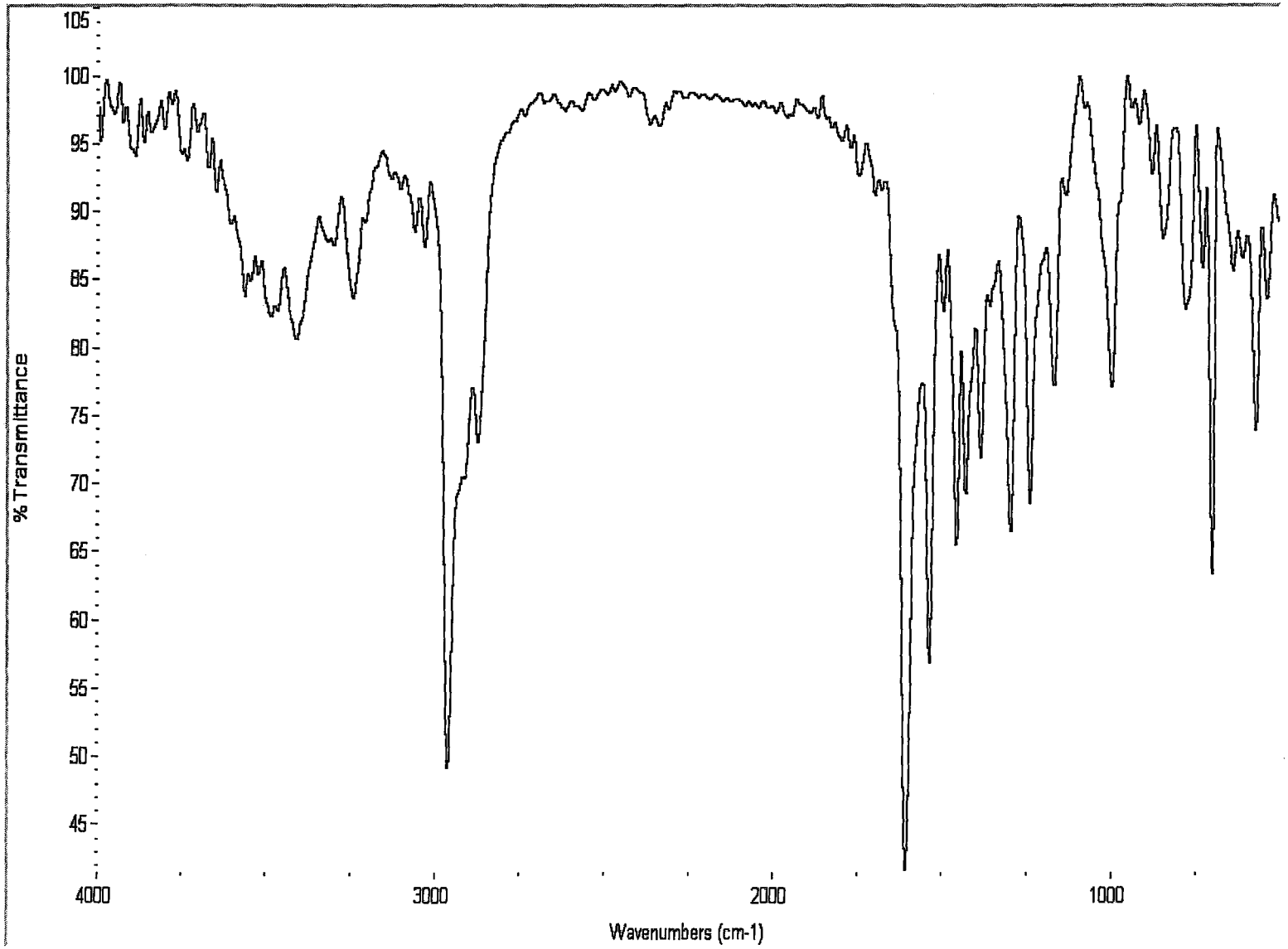
Appendix M

(R,R)-N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-diphenylethylenediamine ferric chlorde complex



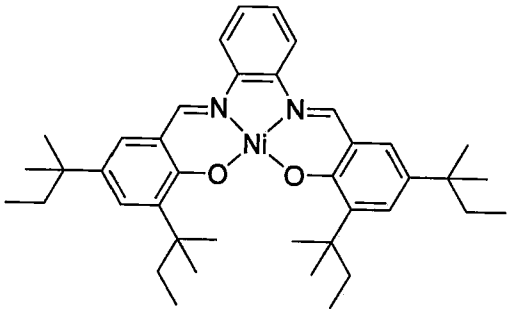
(21)

FT-IR


105
100
95
90
85
80
75
70
65
60
55
50
45
% Transmittance
4000
3000
2000
1000
Wavenumbers (cm-1)

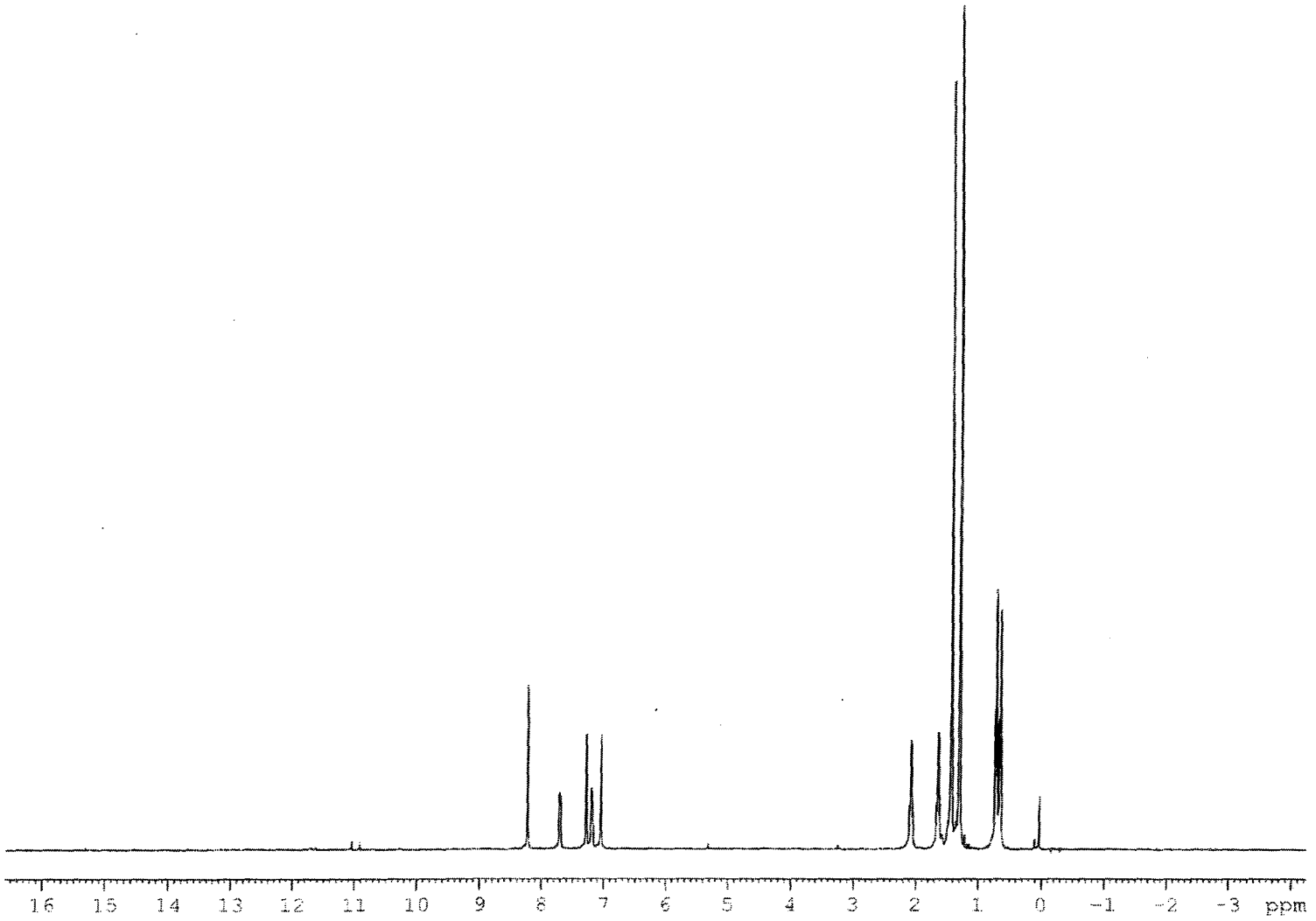
Appendix N

N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-phenylenediami
nickel (II) complex

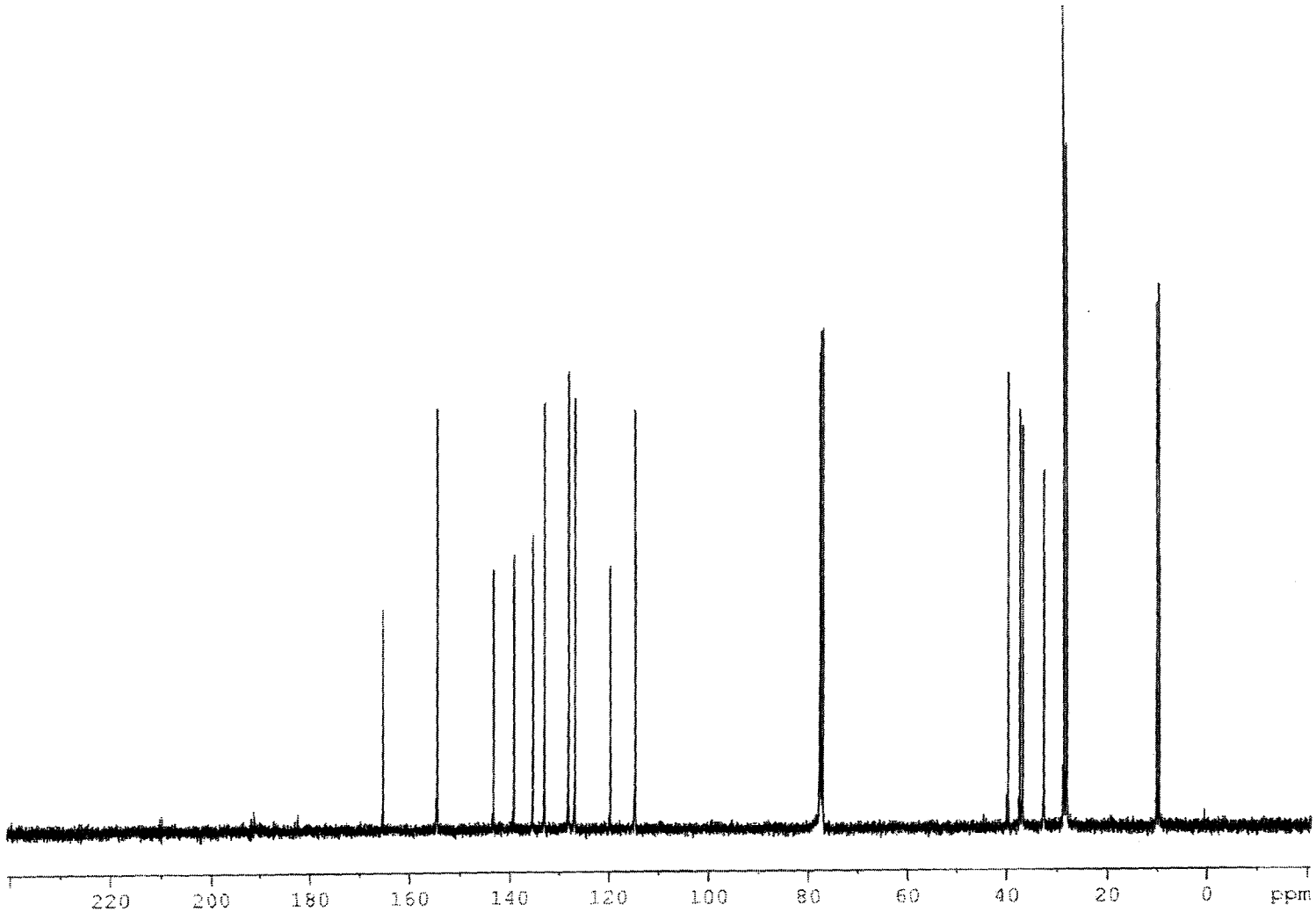


(22)

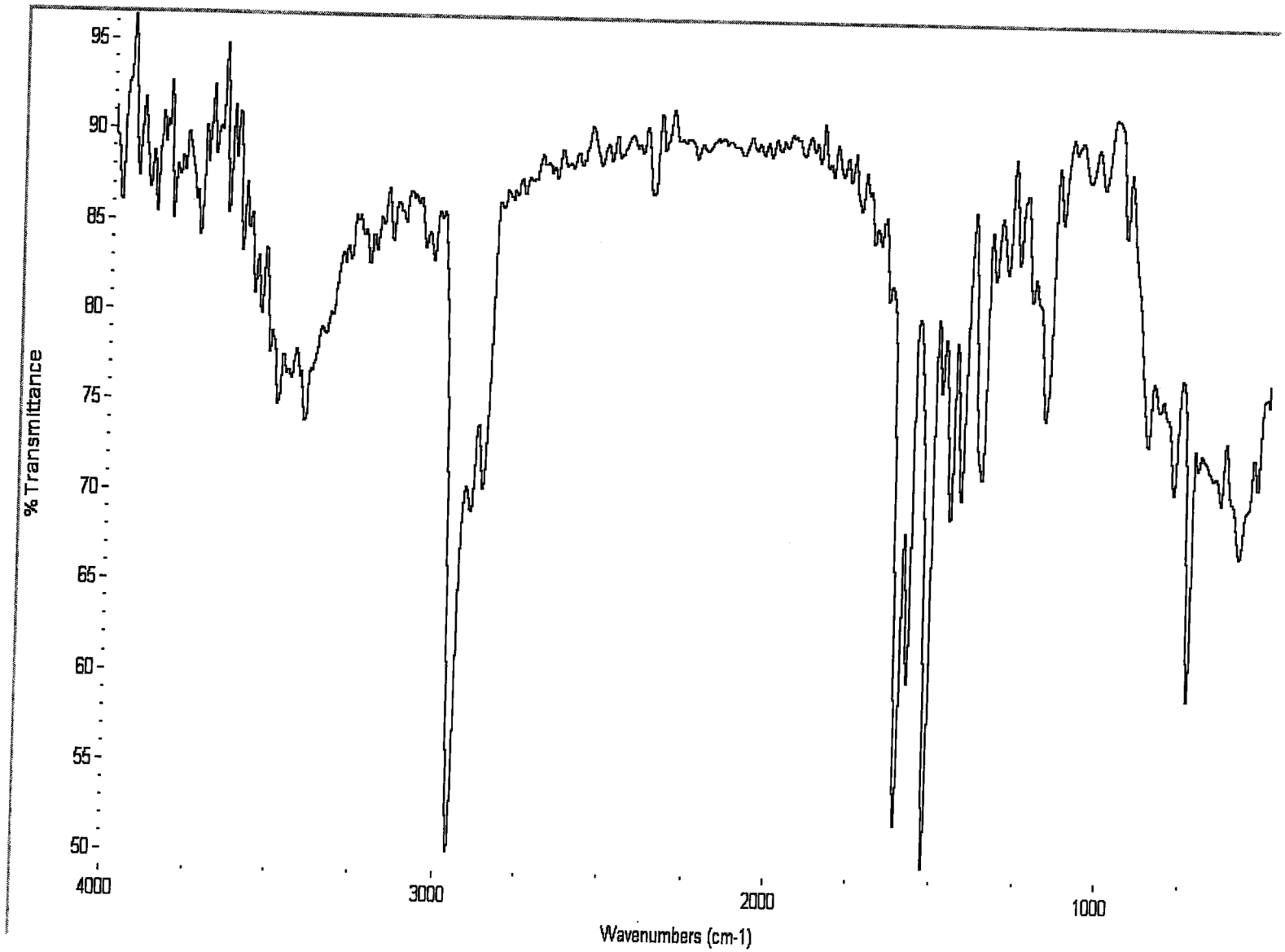
^{1}H NMR
^{13}C NMR
FT-IR



Proton NMR for N,N'−Bis(3,5−di−t−pentylsalicyldene)−1,2−phenylenediamine nickel (II) complex

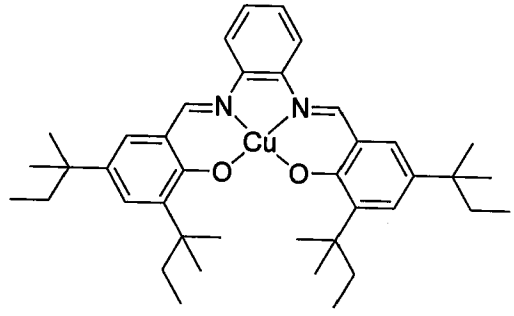


Carbon 13 NMR for N,N'–Bis(3,5–di–t–pentylsalicyldene)–1,2–phenylenediamine nickel (II) complex


95
90
85
80
75
70
65
60
55
50
% Transmittance
4000
3000
2000
1000
Wavenumbers (cm-1)

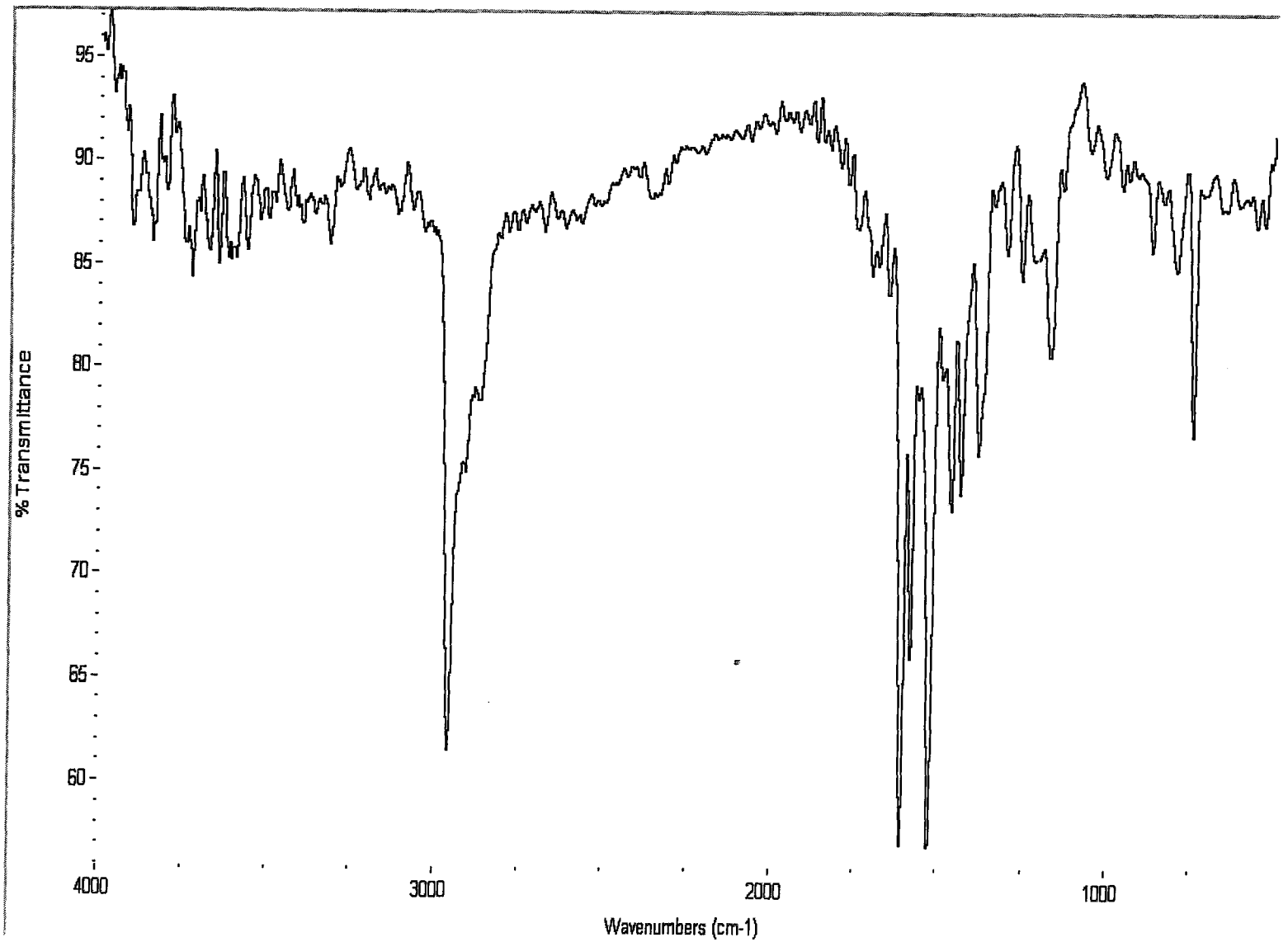
Appendix O

N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-phenylenediamine copper (II) complex



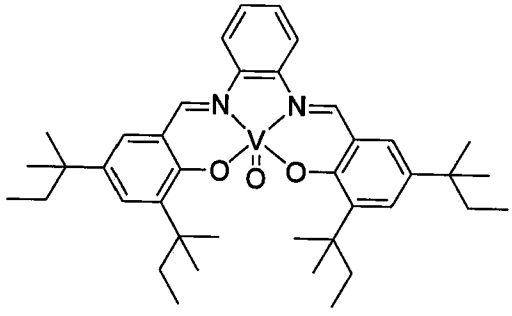
(23)

FT-IR


% Transmittance
95
90
85
80
75
70
65
60
4000
3000
2000
1000
Wavenumbers (cm-1)

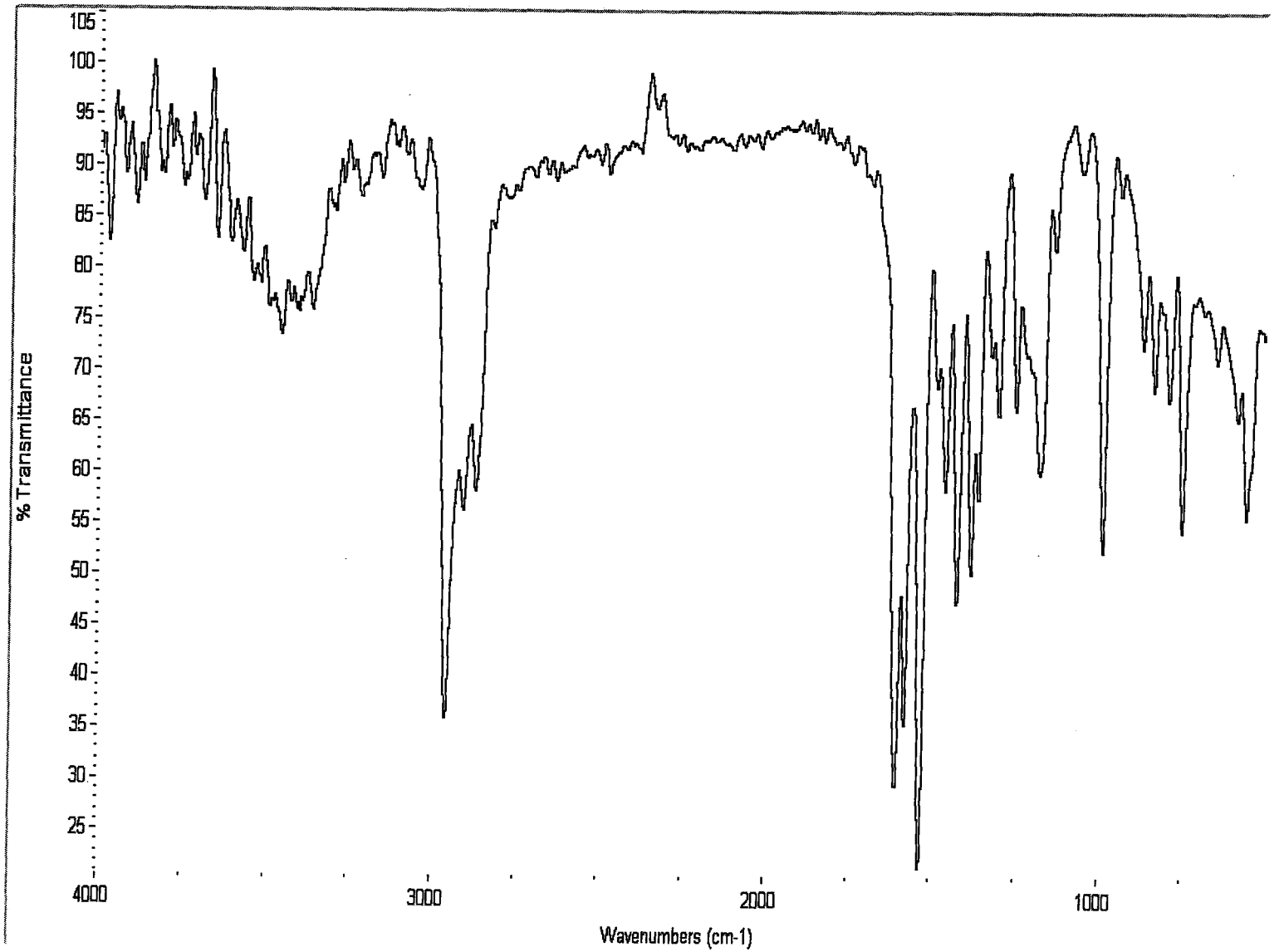
Appendix P

N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-phenylenediam vanadyl (II) complex



(24)

FT-IR


105
100
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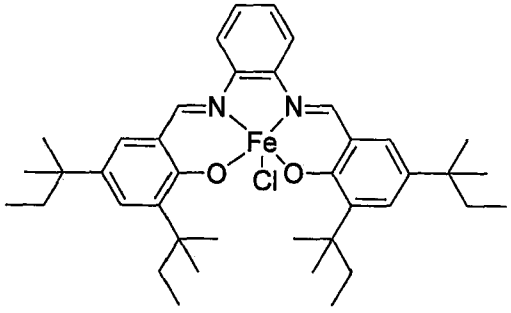
85
80
75
70
65
60
55
50
45
40
35
30
25
% Transmittance
4000
3000
2000
1000
Wavenumbers (cm-1)

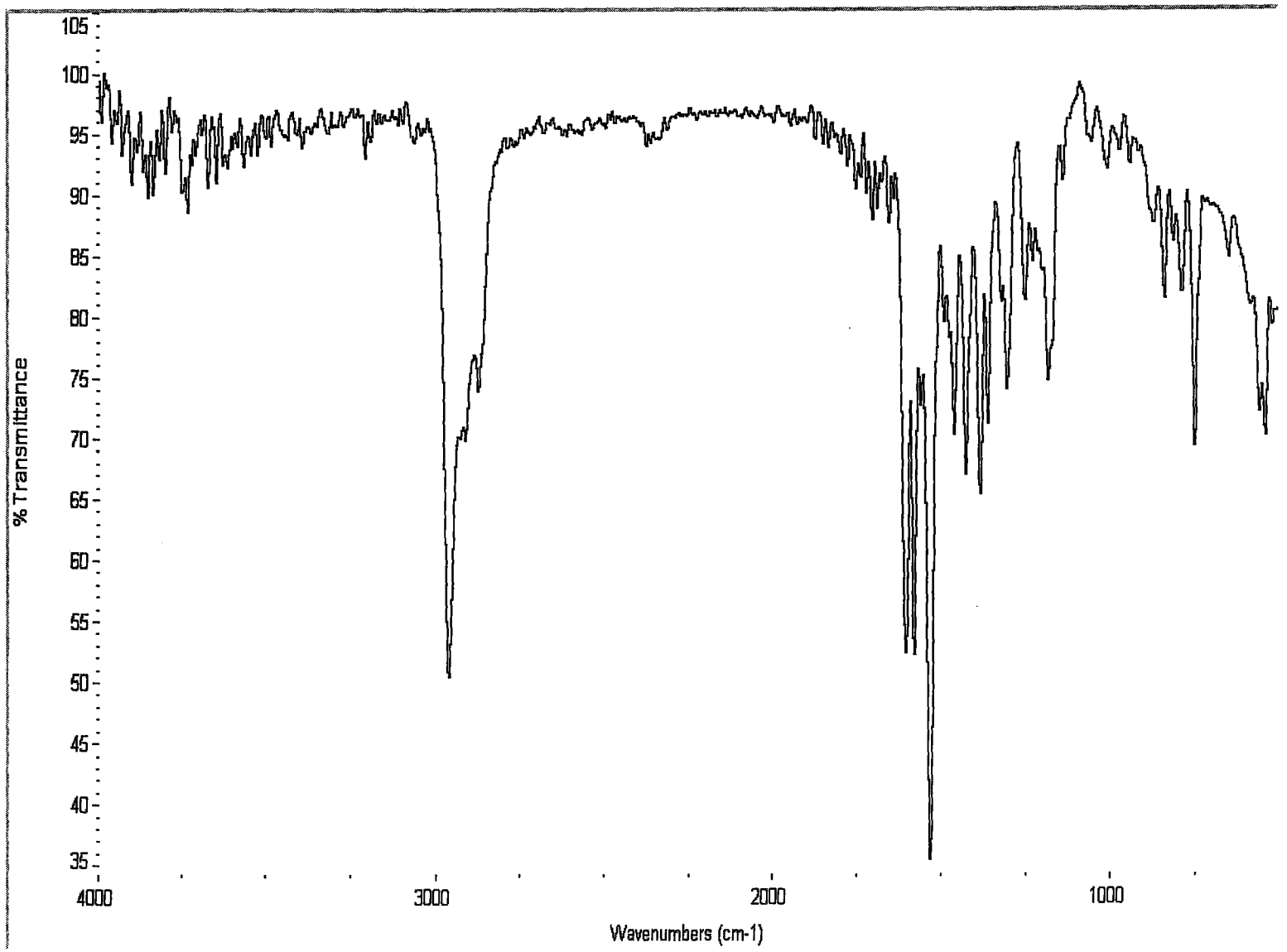
Appendix Q

N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-phenylenediamine ferric chloride complex



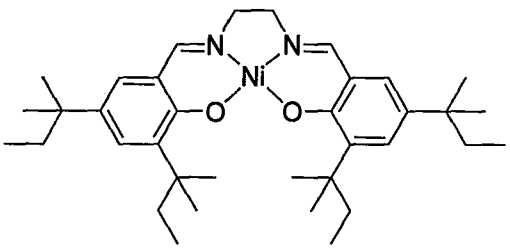
(25)

FT-IR


105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
% Transmittance
4000
3000
2000
1000
Wavenumbers (cm-1)

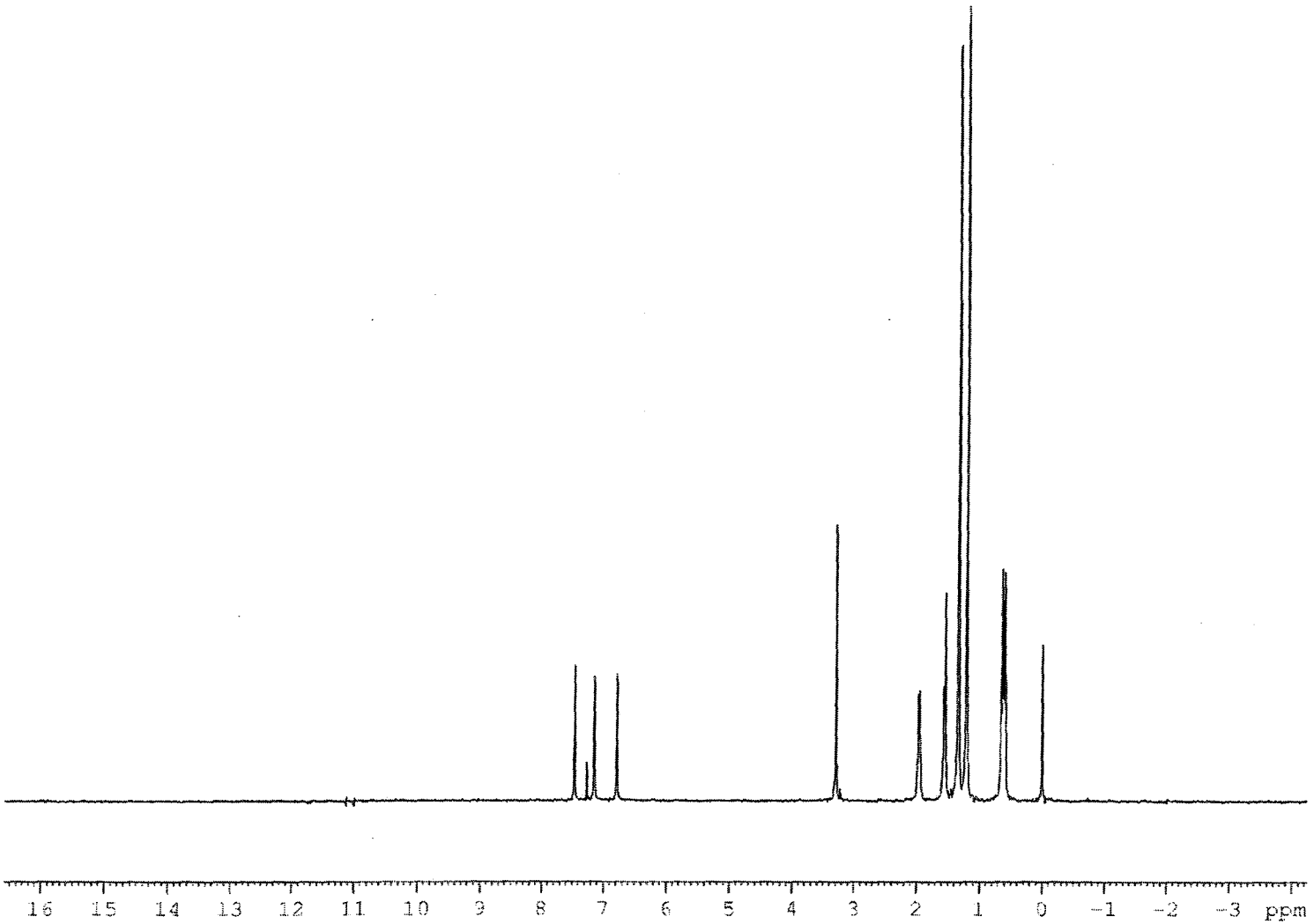
Appendix R

N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-ethylenediamine nickel (II) complex

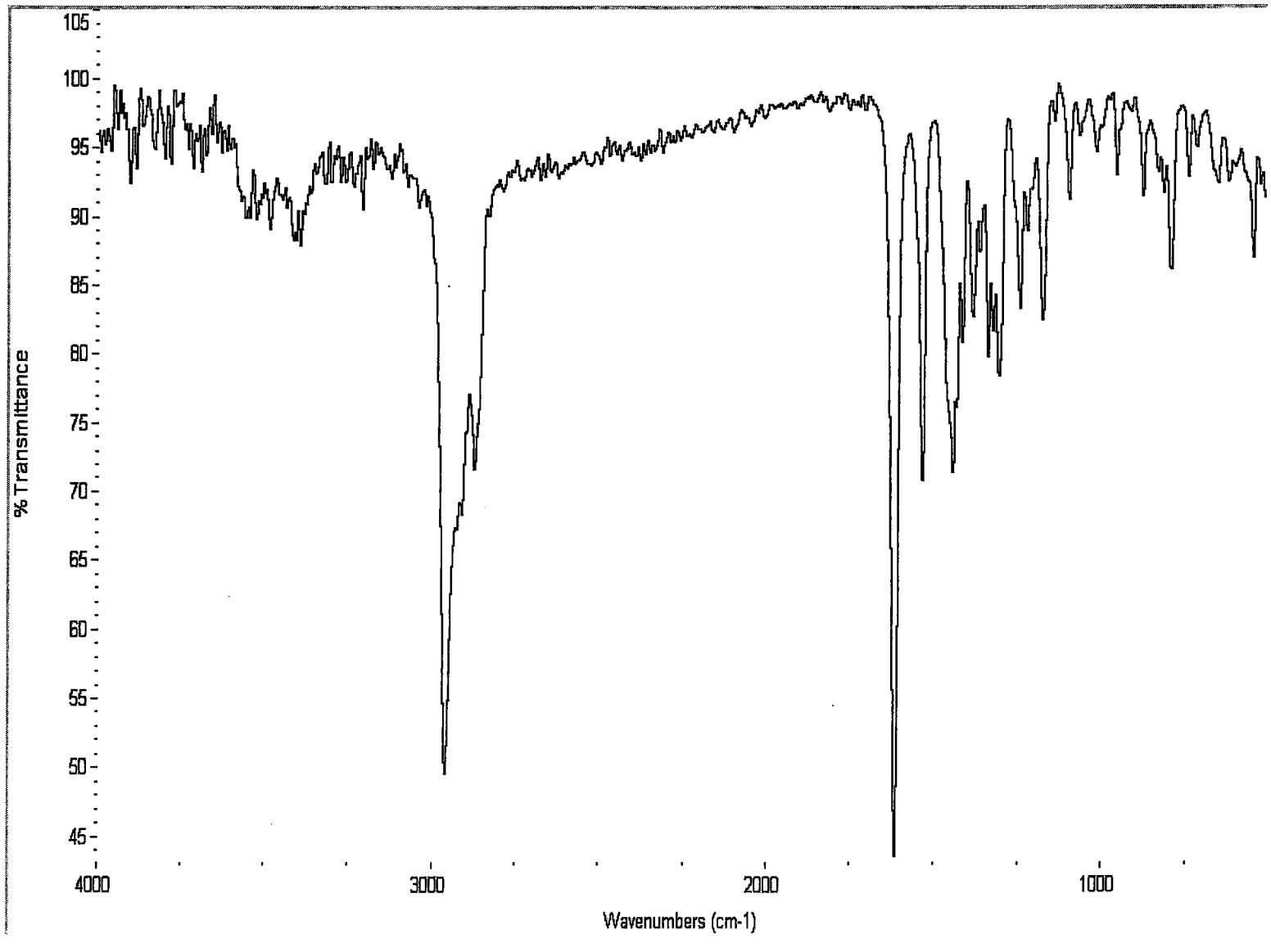


(26)

^{1}H NMR
FT-IR
UV

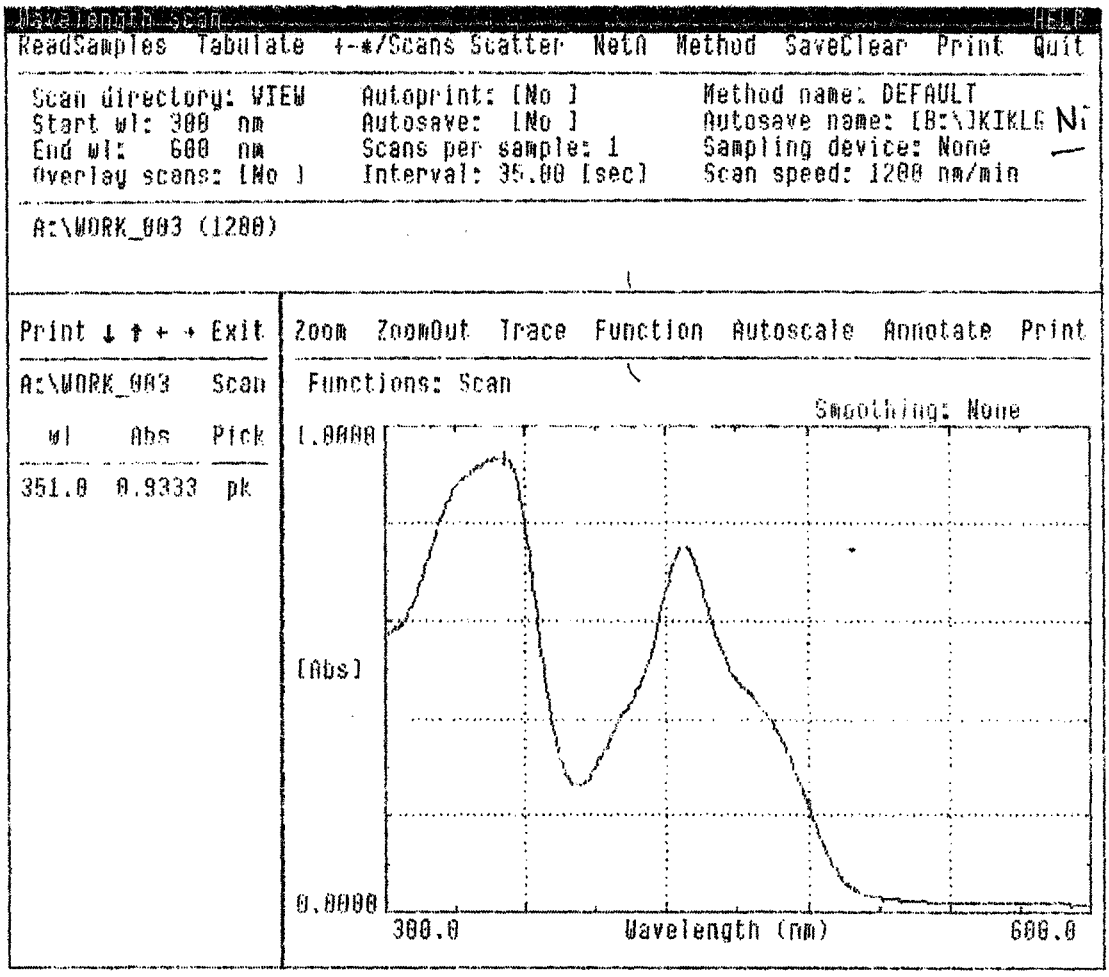


Proton NMR for N,N'−Bis(3,5−di−t−pentylsalicylidene)−1,2−ethylenediamine nickel (II) complex


105
100
95
90
85
80
75
70
65
60
55
50
45
% Transmittance
4000
3000
2000
1000
Wavenumbers (cm-1)

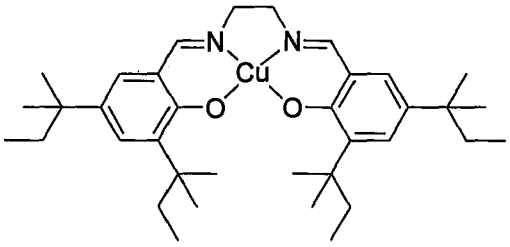
RCMI Facilities: Clark Atlanta Univerity

Date: 07/15/04
Time: 03:22



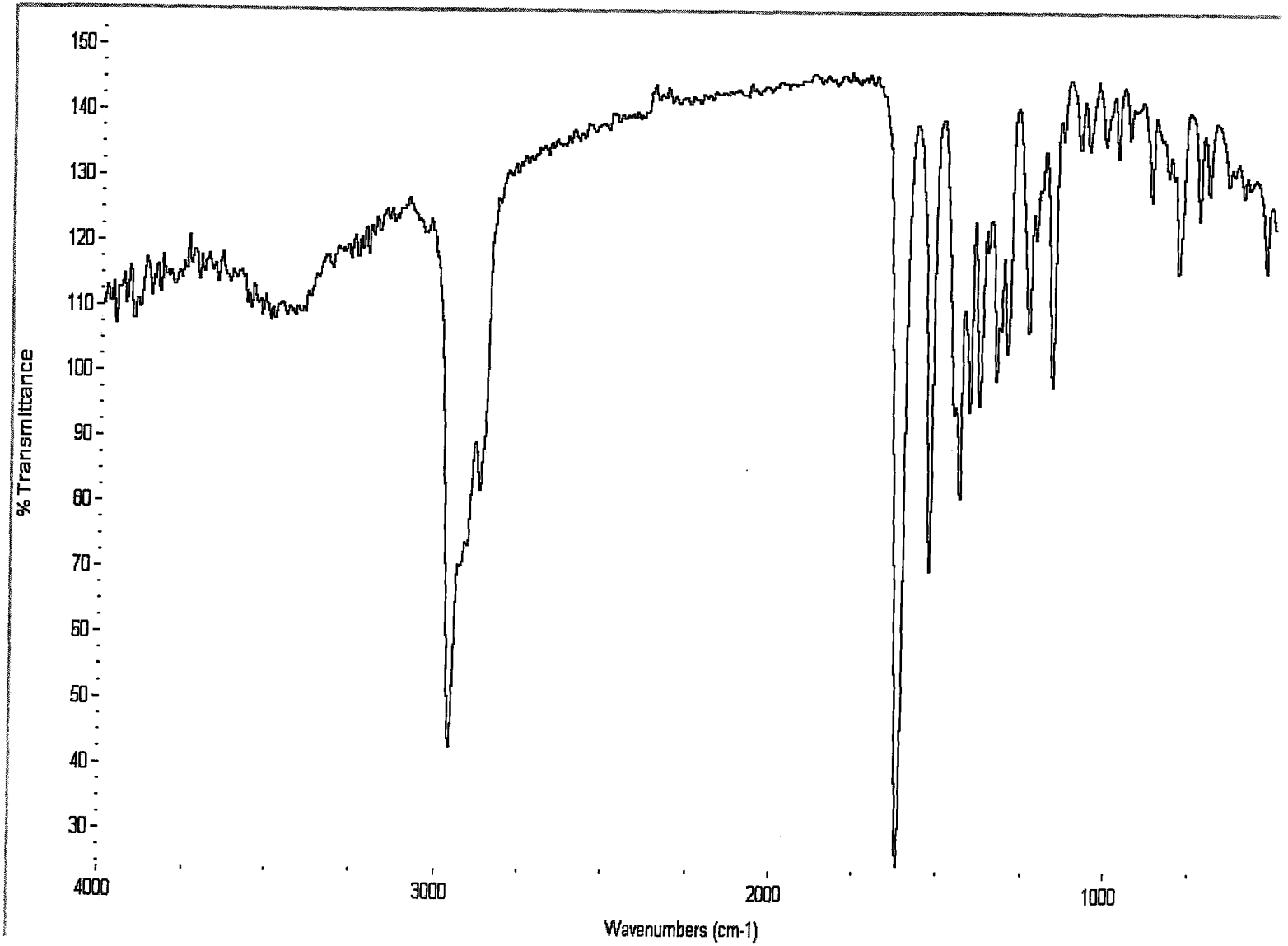
Appendix S

N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-ethylenediamine copper (II) complex



(27)

FT-IR
UV
X-RAY


150
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110
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90
80
70
60
50
40
30
% Transmittance
4000
3000
2000
1000
Wavenumbers (cm-1)

RCMI Facilities: Clark Atlanta Univerity

Date: 07/15/04
Time: 03:39

Wavelength Scan HELP

ReadSamples Tabulate +-*/Scans Scatter NetA Method SaveClear Print Quit

Scan directory: VIEW
Start wl: 300 nm
End wl: 600 nm
Overlay scans: [No]

Autoprint: [No]
Autosave: [No]
Scans per sample: 1
Interval: 35.00 [sec]

Method name: DEFAULT
Autosave name: [B:\]KIKLG
Sampling device: None
Scan speed: 1200 nm/min

A:\WORK_003 (1200)

Print ↓ ↑ ← → Exit

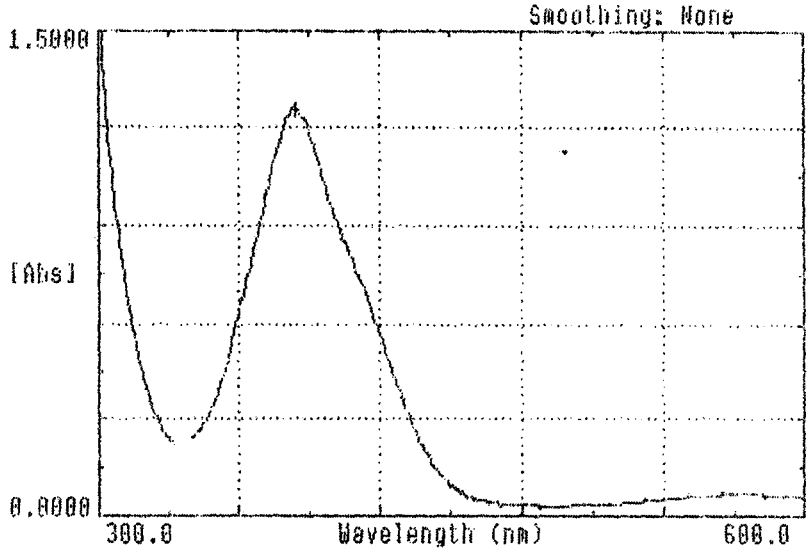
A:\WORK_003 Scan

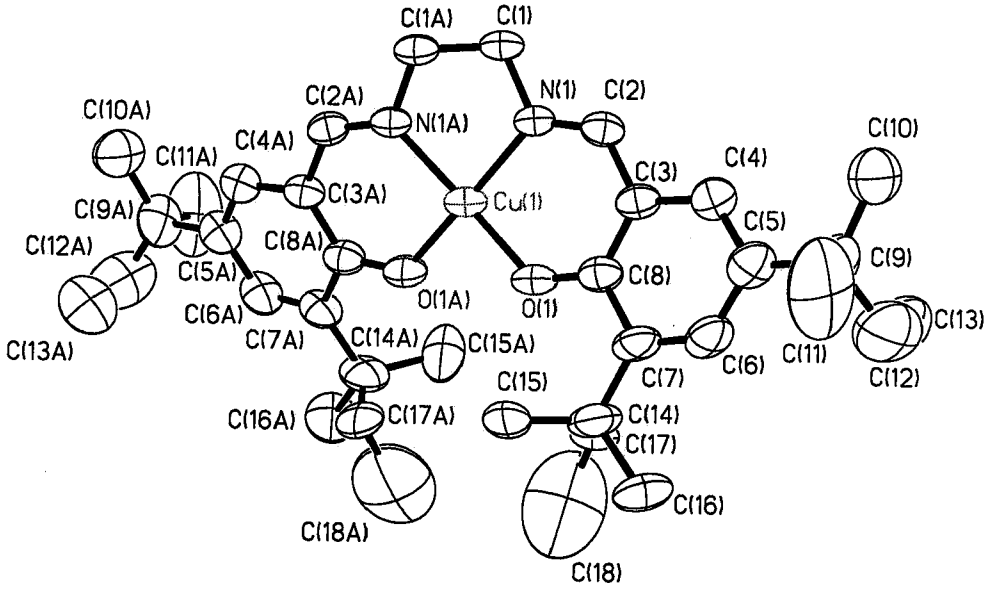
wl	Abs	Pick
384.0	1.2518	pk

Zoom ZoomOut Trace Function Autoscale Annotate Print

Functions: Scan

Smoothing: None

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C(1)
C(10A)
C(2A)
N(1A)
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C(2)
C(10)
C(4A)
C(11A)
C(3A)
Cu(1)
C(3)
C(4)
C(9A)
C(5A)
C(8A)
C(5)
C(12A)
C(9)
O(1A)
O(1)
C(8)
C(6A)
C(7A)
C(14A)
C(15A)
C(13A)
C(11)
C(13)
C(7)
C(6)
C(12)
C(15)
C(16A)
C(17A)
C(14)
C(17)
C(16)
C(18A)
C(18)

N,N'-Bis(3,5-di-t-pentylsalicylidene)-1,2-ethylenediamine copper (II) complex (CIF File)

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 'H'  'H'   0.0000   0.0000
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 'N'  'N'   0.0061   0.0033
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 'O'  'O'   0.0106   0.0060
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 'Cl'  'Cl'   0.1484   0.1585
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 '-x+1/2, -y, z+1/2'
 '-x, y+1/2, -z+1/2'
 'x+1/2, -y+1/2, -z'

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_cell_length_b                    12.790(3)
_cell_length_c                    29.387(6)
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_cell_angle_beta                  90.00
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_cell_volume                       3601.4(13)
_cell_formula_units_Z              5
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_cell_measurement_theta_min        ?
_cell_measurement_theta_max        ?

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_exptl_special_details
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 ?
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_diffrn_radiation_type             MoK\a
_diffrn_radiation_source           'fine-focus sealed tube'
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_diffrn_standards_interval_time    ?
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_computing_cell_refinement        ?
_computing_data_reduction         ?
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_computing_structure_refinement   'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics     ?
_computing_publication_material   ?

_refine_special_details
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR
and
 goodness of fit S are based on F^2^, conventional R-factors R are
based
 on F, with F set to zero for negative F^2^. The threshold expression
of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc.
and is
 not relevant to the choice of reflections for refinement.  R-factors
based
 on F^2^ are statistically about twice as large as those based on F,
and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.1163P)^2^+0.0000P] where
P=(Fo^2^+2Fc^2^)/3'
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_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
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_refine_ls_extinction_method      none
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 'Flack H D (1983), Acta Cryst. A39, 876-881'
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_refine_ls_number_parameters      385
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_refine_ls_goodness_of_fit_ref   1.038
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 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
 _atom_site_calc_flag
 _atom_site_refinement_flags
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Cl1 Cl 0.3018(2) 0.9809(2) 0.01866(7) 0.0763(7) Uani 1 1 d . . .
O2 O 0.2914(4) 0.9708(4) 0.12943(15) 0.0521(13) Uani 1 1 d . . .
O1 O 0.2860(4) 0.7720(4) 0.08941(17) 0.0491(12) Uani 1 1 d . . .
N2 N 0.5619(5) 0.9714(5) 0.10264(18) 0.0433(13) Uani 1 1 d . . .
N1 N 0.5357(6) 0.8140(5) 0.05033(19) 0.0503(15) Uani 1 1 d . . .
C1 C 0.6568(7) 0.8769(6) 0.0390(3) 0.057(2) Uani 1 1 d . . .
H1A H 0.6358 0.9241 0.0145 0.092 Uiso 1 1 calc R . .
H1B H 0.7337 0.8333 0.0301 0.092 Uiso 1 1 calc R . .
C2 C 0.6905(7) 0.9358(6) 0.0814(3) 0.0604(19) Uani 1 1 d . . .
H2A H 0.7407 0.8914 0.1020 0.097 Uiso 1 1 calc R . .
H2B H 0.7485 0.9948 0.0742 0.097 Uiso 1 1 calc R . .
C3 C 0.5720(7) 1.0392(6) 0.1342(2) 0.0463(16) Uani 1 1 d . . .
H3 H 0.6644 1.0640 0.1407 0.045(18) Uiso 1 1 calc R . .
C4 C 0.4604(6) 1.0834(5) 0.1616(2) 0.0406(15) Uani 1 1 d . . .
C5 C 0.4943(7) 1.1615(7) 0.1921(2) 0.056(2) Uani 1 1 d . . .
H5 H 0.5904 1.1816 0.1952 0.048(19) Uiso 1 1 calc R . .
C6 C 0.3960(9) 1.2114(7) 0.2182(3) 0.071(2) Uani 1 1 d . . .
C7 C 0.2576(8) 1.1784(7) 0.2119(3) 0.059(2) Uani 1 1 d . . .
H7 H 0.1865 1.2125 0.2295 0.036(16) Uiso 1 1 calc R . .
C8 C 0.2163(7) 1.1004(7) 0.1823(2) 0.0512(17) Uani 1 1 d . . .
C9 C 0.3227(7) 1.0482(5) 0.1563(2) 0.0412(15) Uani 1 1 d . . .
C10 C 0.3041(7) 0.6749(5) 0.0772(2) 0.0413(14) Uani 1 1 d . . .
C11 C 0.2049(7) 0.5970(6) 0.0878(2) 0.0477(15) Uani 1 1 d . . .
C12 C 0.2349(8) 0.4954(6) 0.0758(3) 0.0583(19) Uani 1 1 d . . .
H12 H 0.1667 0.4432 0.0832 0.10(3) Uiso 1 1 calc R . .
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C13 C 0.3547(8) 0.4622(5) 0.0540(2) 0.0517(18) Uani 1 1 d . . .
C14 C 0.4469(7) 0.5369(5) 0.0420(3) 0.0481(17) Uani 1 1 d . . .
H14 H 0.5282 0.5171 0.0249 0.004(11) Uiso 1 1 calc R . .
C15 C 0.4286(8) 0.6428(6) 0.0534(2) 0.0495(17) Uani 1 1 d . . .
C16 C 0.5356(7) 0.7138(6) 0.0424(2) 0.0458(16) Uani 1 1 d . . .
H16 H 0.6166 0.6856 0.0276 0.037(15) Uiso 1 1 calc R . .
C17 C 0.4285(10) 1.2947(11) 0.2534(4) 0.117(5) Uani 1 1 d . . .
C18 C 0.5768(13) 1.3326(16) 0.2511(7) 0.231(13) Uani 1 1 d . . .
H18A H 0.5933 1.3818 0.2751 0.369 Uiso 1 1 calc R . .
H18B H 0.5927 1.3659 0.2223 0.369 Uiso 1 1 calc R . .
H18C H 0.6391 1.2743 0.2543 0.369 Uiso 1 1 calc R . .
C19 C 0.3442(19) 1.4004(13) 0.2332(9) 0.213(11) Uani 1 1 d . . .
H19A H 0.2486 1.3826 0.2271 0.341 Uiso 1 1 calc R . .
H19B H 0.3881 1.4234 0.2056 0.341 Uiso 1 1 calc R . .
H19C H 0.3477 1.4554 0.2554 0.341 Uiso 1 1 calc R . .
C20 C 0.369(2) 1.285(2) 0.2959(8) 0.228(14) Uani 1 1 d . . .
H20A H 0.2700 1.2768 0.2936 0.365 Uiso 1 1 calc R . .
H20B H 0.3894 1.3450 0.3143 0.365 Uiso 1 1 calc R . .
C21 C 0.437(4) 1.185(3) 0.3164(7) 0.260(17) Uani 1 1 d . . .
H21A H 0.3804 1.1255 0.3096 0.417 Uiso 1 1 calc R . .
H21B H 0.4455 1.1930 0.3488 0.417 Uiso 1 1 calc R . .
H21C H 0.5285 1.1756 0.3034 0.417 Uiso 1 1 calc R . .
C22 C 0.0624(8) 1.0729(8) 0.1749(3) 0.071(3) Uani 1 1 d . . .
C23 C 0.0243(9) 1.0854(15) 0.1250(4) 0.125(6) Uani 1 1 d . . .
H23A H -0.0568 1.0440 0.1183 0.200 Uiso 1 1 calc R . .
H23B H 0.1008 1.0625 0.1064 0.200 Uiso 1 1 calc R . .
H23C H 0.0048 1.1576 0.1187 0.200 Uiso 1 1 calc R . .
C24 C -0.0340(8) 1.1511(10) 0.2019(4) 0.101(4) Uani 1 1 d . . .
H24A H -0.1292 1.1282 0.2000 0.162 Uiso 1 1 calc R . .
H24B H -0.0258 1.2198 0.1890 0.162 Uiso 1 1 calc R . .
H24C H -0.0055 1.1529 0.2333 0.162 Uiso 1 1 calc R . .
C25 C 0.0279(13) 0.9673(12) 0.1820(7) 0.132(6) Uani 1 1 d . . .
H25A H 0.0774 0.9239 0.1608 0.211 Uiso 1 1 calc R . .
H25B H -0.0704 0.9569 0.1775 0.211 Uiso 1 1 calc R . .
C26 C 0.0692(16) 0.9379(13) 0.2318(7) 0.155(6) Uani 1 1 d . . .
H26A H 0.1689 0.9401 0.2349 0.249 Uiso 1 1 calc R . .
H26B H 0.0363 0.8688 0.2386 0.249 Uiso 1 1 calc R . .
H26C H 0.0277 0.9869 0.2526 0.249 Uiso 1 1 calc R . .
C27 C 0.0664(9) 0.6269(7) 0.1126(3) 0.065(2) Uani 1 1 d . . .
C28 C -0.0112(9) 0.7068(9) 0.0842(4) 0.091(3) Uani 1 1 d . . .
H28A H 0.0522 0.7606 0.0746 0.146 Uiso 1 1 calc R . .
H28B H -0.0848 0.7373 0.1019 0.146 Uiso 1 1 calc R . .
H28C H -0.0503 0.6732 0.0579 0.146 Uiso 1 1 calc R . .
C29 C -0.0318(11) 0.5289(9) 0.1168(5) 0.122(5) Uani 1 1 d . . .
H29A H -0.1191 0.5496 0.1300 0.195 Uiso 1 1 calc R . .
H29B H 0.0118 0.4773 0.1358 0.195 Uiso 1 1 calc R . .
H29C H -0.0479 0.4999 0.0871 0.195 Uiso 1 1 calc R . .
C30 C 0.1083(13) 0.6744(11) 0.1587(3) 0.093(4) Uani 1 1 d . . .
H30A H 0.1772 0.7277 0.1538 0.150 Uiso 1 1 calc R . .
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H30B H 0.0281 0.7066 0.1724 0.150 Uiso 1 1 calc R . .
C31 C 0.154(5) 0.610(3) 0.1840(9) 0.39(3) Uani 1 1 d . . .
H31A H 0.2505 0.6247 0.1902 0.627 Uiso 1 1 calc R . .
H31B H 0.1465 0.5419 0.1702 0.627 Uiso 1 1 calc R . .
H31C H 0.1023 0.6106 0.2119 0.627 Uiso 1 1 calc R . .
C32 C 0.3845(12) 0.3472(6) 0.0437(3) 0.073(2) Uani 1 1 d . . .
C33 C 0.381(2) 0.3270(11) -0.0058(4) 0.177(8) Uani 1 1 d . . .
H33A H 0.4146 0.2578 -0.0118 0.284 Uiso 1 1 calc R . .
H33B H 0.4383 0.3771 -0.0212 0.284 Uiso 1 1 calc R . .
H33C H 0.2863 0.3331 -0.0165 0.284 Uiso 1 1 calc R . .
C34 C 0.2907(16) 0.2733(8) 0.0718(6) 0.148(6) Uani 1 1 d . . .
H34A H 0.1955 0.2810 0.0623 0.236 Uiso 1 1 calc R . .
H34B H 0.2983 0.2906 0.1035 0.236 Uiso 1 1 calc R . .
H34C H 0.3199 0.2023 0.0672 0.236 Uiso 1 1 calc R . .
C35 C 0.5322(19) 0.3198(13) 0.0580(7) 0.159(7) Uani 1 1 d . . .
H35A H 0.5431 0.2462 0.0525 0.254 Uiso 1 1 calc R . .
H35B H 0.5930 0.3548 0.0370 0.254 Uiso 1 1 calc R . .
C36 C 0.585(2) 0.3376(18) 0.0995(8) 0.195(10) Uani 1 1 d . . .
H36A H 0.6155 0.4088 0.1015 0.312 Uiso 1 1 calc R . .
H36B H 0.6620 0.2915 0.1048 0.312 Uiso 1 1 calc R . .
H36C H 0.5137 0.3251 0.1220 0.312 Uiso 1 1 calc R . .

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O2 0.046(3) 0.053(3) 0.057(3) -0.022(3) 0.007(2) -0.019(2)
O1 0.048(3) 0.032(2) 0.068(3) -0.010(2) 0.013(2) -0.003(2)
N2 0.046(3) 0.041(3) 0.043(3) -0.012(3) 0.008(2) -0.003(3)
N1 0.052(3) 0.046(4) 0.054(3) -0.005(3) 0.021(3) -0.012(3)
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C2 0.054(4) 0.048(4) 0.079(5) -0.022(4) 0.011(4) -0.011(3)
C3 0.044(4) 0.041(4) 0.054(4) -0.002(3) 0.003(3) -0.010(3)
C4 0.040(3) 0.036(4) 0.046(3) -0.004(3) -0.005(3) -0.004(3)
C5 0.046(4) 0.058(5) 0.063(5) -0.025(4) -0.007(4) -0.008(4)
C6 0.061(5) 0.071(6) 0.079(5) -0.042(5) -0.008(4) -0.003(5)
C7 0.043(4) 0.065(5) 0.070(5) -0.035(4) 0.003(4) 0.000(4)
C8 0.048(4) 0.056(4) 0.050(3) -0.017(4) 0.002(3) -0.005(4)
C9 0.054(4) 0.032(3) 0.037(3) -0.005(3) -0.007(3) -0.002(3)
C10 0.049(3) 0.028(3) 0.047(3) -0.004(3) 0.002(3) -0.004(3)
C11 0.052(4) 0.033(3) 0.058(4) -0.008(4) 0.011(3) -0.006(3)
C12 0.062(4) 0.043(4) 0.071(5) -0.006(4) 0.007(4) -0.008(4)
C13 0.054(4) 0.038(4) 0.062(4) -0.007(4) 0.005(4) -0.002(4)
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C14 0.048(4) 0.033(4) 0.063(4) -0.008(3) 0.016(3) 0.003(3)
C15 0.054(4) 0.047(4) 0.047(4) -0.005(3) 0.011(3) -0.002(3)
C16 0.049(4) 0.042(4) 0.047(3) -0.011(3) 0.015(3) -0.002(3)
C17 0.076(7) 0.144(12) 0.129(9) -0.112(9) 0.014(6) -0.025(7)
C18 0.098(9) 0.28(2) 0.31(2) -0.25(2) 0.017(11) -0.069(12)
C19 0.192(17) 0.095(11) 0.35(3) -0.123(17) 0.009(18) 0.034(12)
C20 0.188(18) 0.30(3) 0.20(2) -0.20(2) 0.039(18) -0.08(2)
C21 0.35(4) 0.31(4) 0.123(14) -0.05(2) -0.067(18) 0.07(3)
C22 0.047(4) 0.077(7) 0.089(6) -0.041(5) 0.015(4) -0.018(4)
C23 0.045(5) 0.225(19) 0.105(8) -0.047(10) -0.017(5) -0.005(8)
C24 0.042(5) 0.133(11) 0.128(8) -0.066(8) 0.015(5) 0.002(5)
C25 0.089(8) 0.085(9) 0.221(17) -0.023(11) 0.062(10) -0.017(7)
C26 0.158(13) 0.101(11) 0.207(17) 0.028(12) 0.037(12) -0.001(10)
C27 0.062(5) 0.049(5) 0.084(5) -0.005(4) 0.028(4) -0.010(4)
C28 0.060(5) 0.073(7) 0.140(9) 0.010(8) 0.007(6) 0.009(5)
C29 0.092(7) 0.067(7) 0.206(14) -0.020(8) 0.072(8) -0.028(6)
C30 0.100(7) 0.102(9) 0.079(7) -0.015(6) 0.054(6) -0.018(7)
C31 0.65(8) 0.35(5) 0.18(2) -0.07(3) 0.17(3) -0.22(6)
C32 0.094(6) 0.031(4) 0.093(6) -0.001(4) 0.026(6) -0.006(5)
C33 0.33(2) 0.072(8) 0.127(10) -0.047(8) 0.054(14) -0.030(15)
C34 0.205(14) 0.036(5) 0.202(16) 0.007(8) 0.077(13) -0.013(7)
C35 0.152(14) 0.080(9) 0.25(2) 0.006(13) 0.007(14) 0.051(10)
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 All esds (except the esd in the dihedral angle between two l.s.
planes)
 are estimated using the full covariance matrix.  The cell esds are
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 into account individually in the estimation of esds in distances,
angles
 and torsion angles; correlations between esds in cell parameters are
only
 used when they are defined by crystal symmetry.  An approximate
(isotropic)
 treatment of cell esds is used for estimating esds involving l.s.
planes.
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C18 C17 C6 112.9(8) . . ?
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C6 C17 C19 103.0(10) . . ?
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C23 C22 C8 110.2(7) . . ?
C25 C22 C24 113.4(9) . . ?
C23 C22 C24 106.2(10) . . ?
C8 C22 C24 110.2(7) . . ?
C22 C25 C26 108.1(14) . . ?
C28 C27 C30 110.3(9) . . ?
C28 C27 C11 108.9(7) . . ?
C30 C27 C11 106.6(7) . . ?
C28 C27 C29 106.7(8) . . ?
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C33 C32 C34 113.9(12) . . ?
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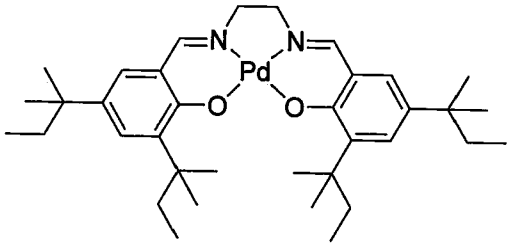
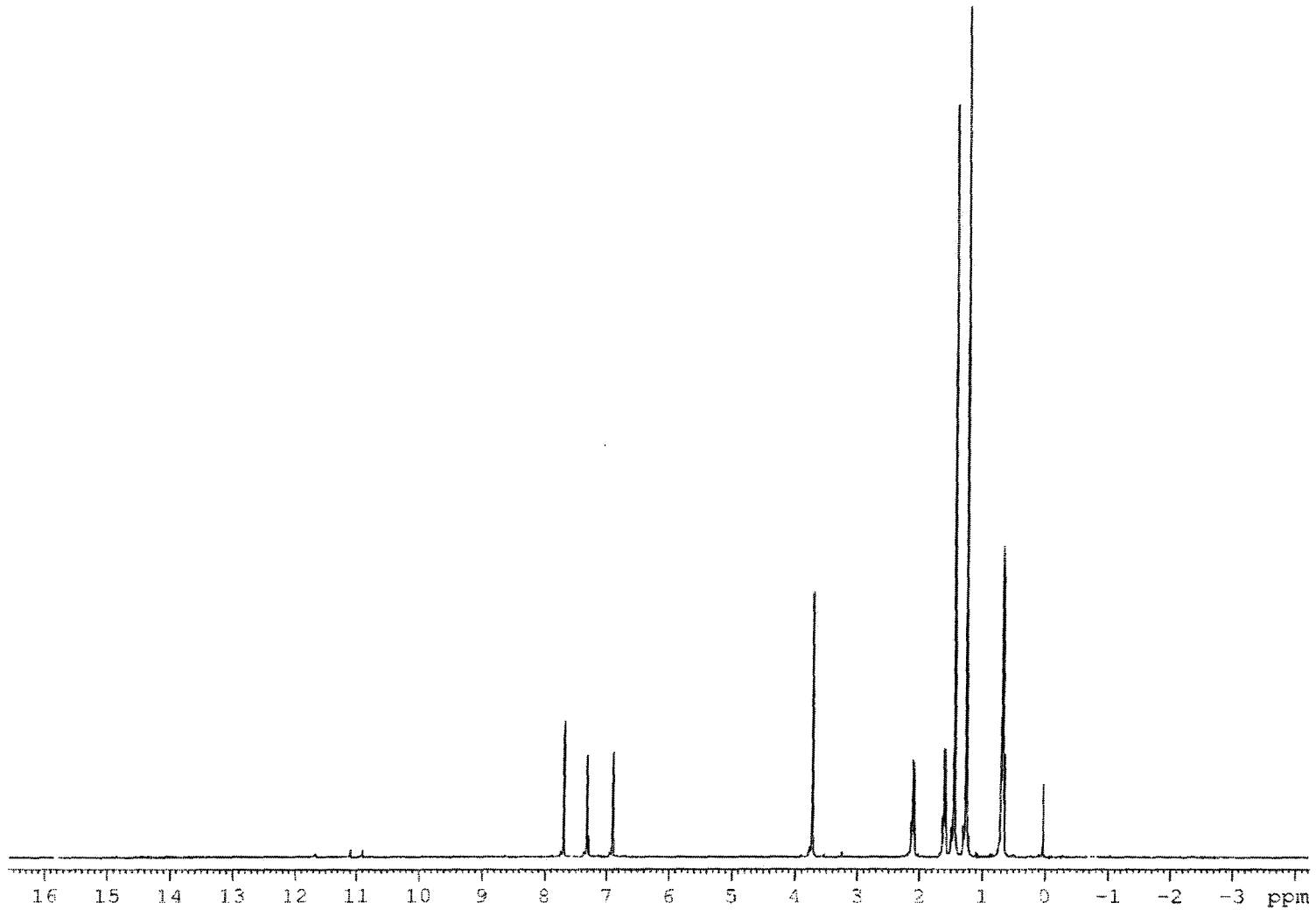
Appendix T

N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-ethylenediamine palladium (II) complex

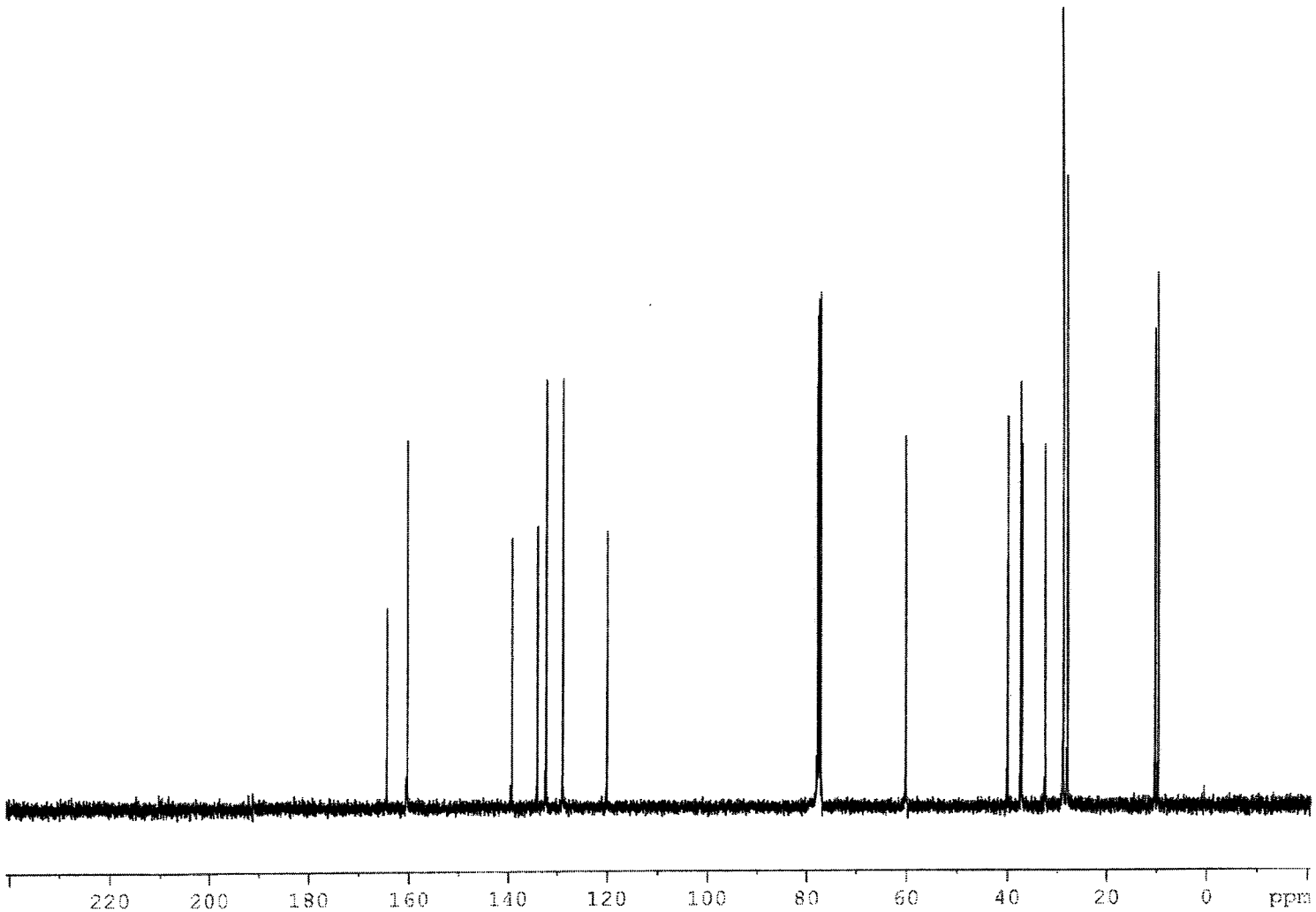


(28)

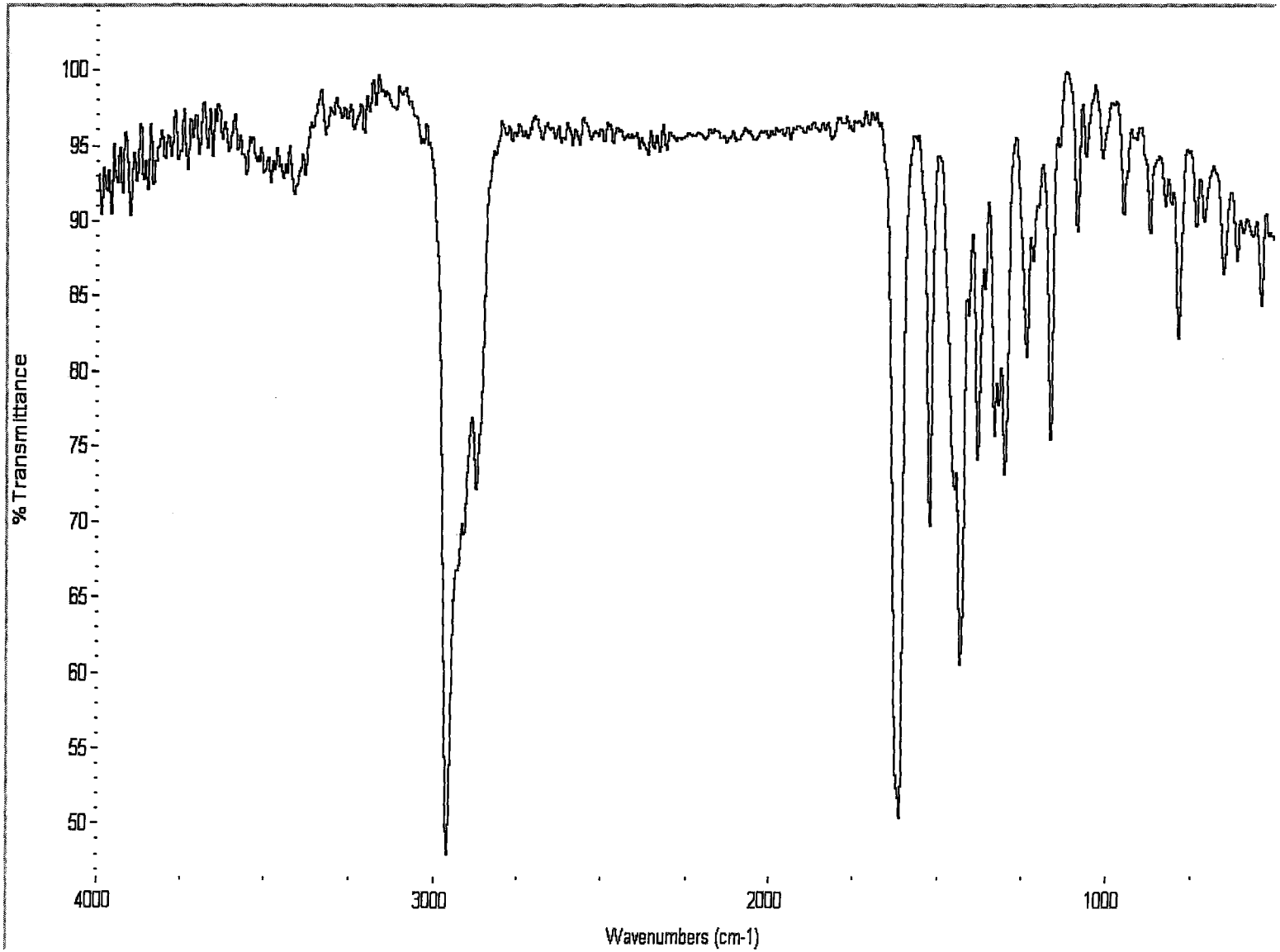
^{1}H NMR
^{13}C NMR
FT-IR
UV



Proton NMR for N,N'–Bis(3,5–di–t–pentylsalicylidene)–1,2–ethylenediamine palladium (II) complex

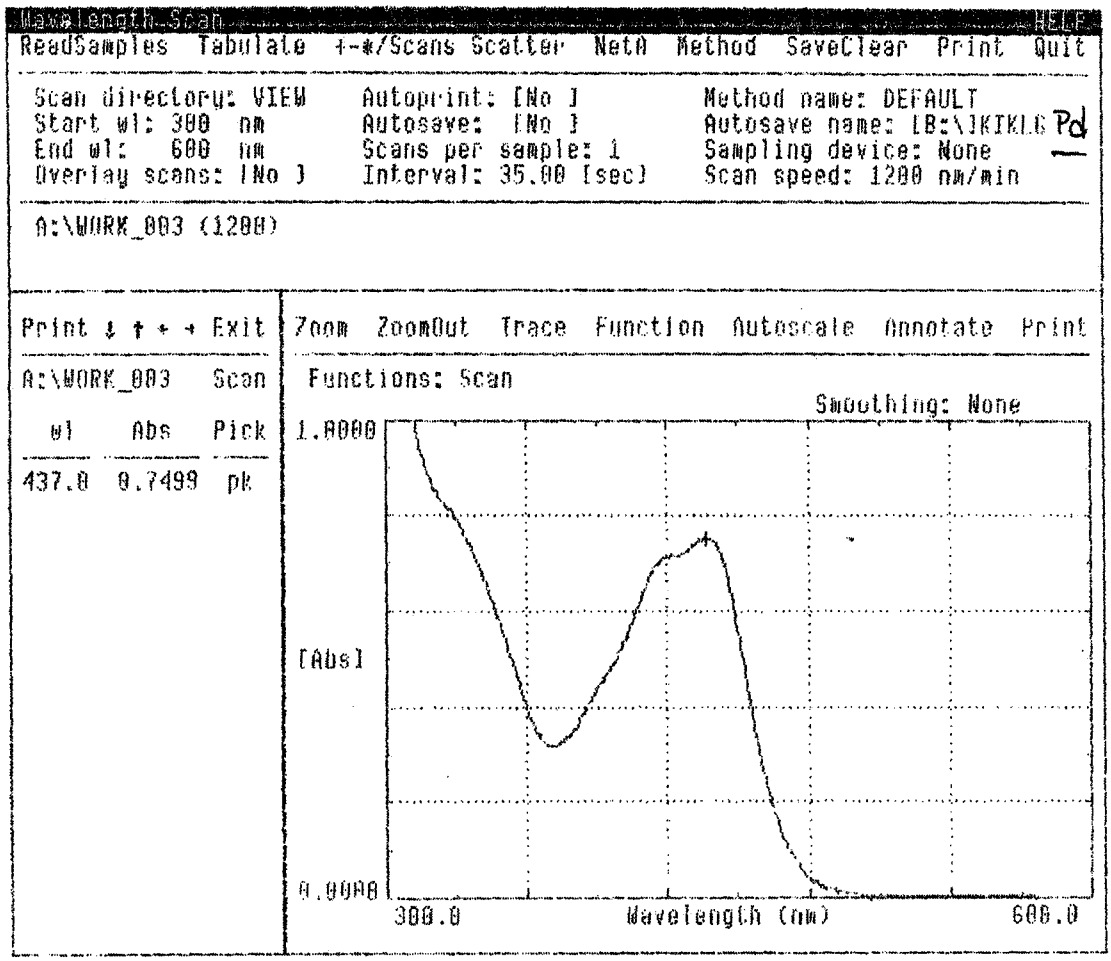


Carbon 13 NMR for N,N'–Bis(3,5–di–t–pentylsalicylidene)–1,2–ethylenediamine palladium (II) complex


100
95
90
85
80
75
70
65
60
55
50
% Transmittance
4000
3000
2000
1000
Wavenumbers (cm-1)

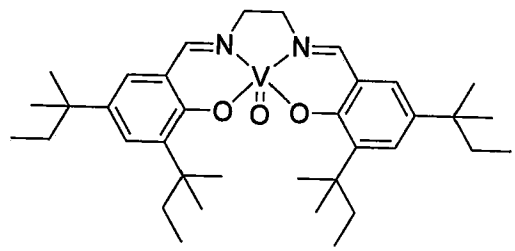
RCMI Facilities: Clark Atlanta Univerity

Date: 07/15/04
Time: 03:56



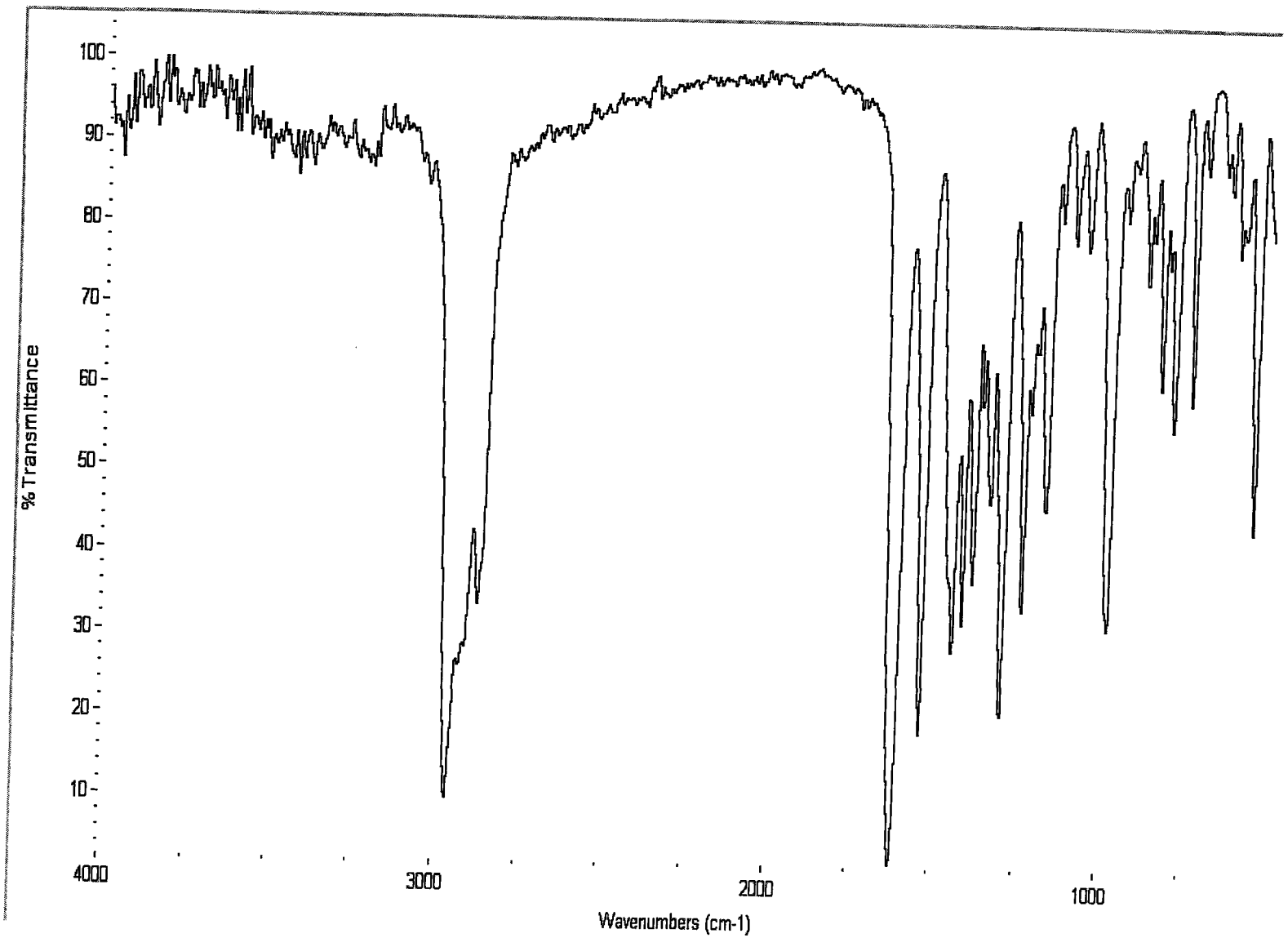
Appendix U

N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-ethylenediamine vanadyl (II) complex



(29)

FT-IR
UV


100
90
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70
60
50
40
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20
10
% Transmittance
4000
3000
2000
1000
Wavenumbers (cm-1)

RCMI Facilities: Clark Atlanta Univerity

Date: 07/15/04
Time: 03:04

Wavelength Scan HELP

ReadSamples Tabulate +-*/Scans Scatter NetA Method SaveClear Print Quit

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End wl: 600 nm
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Print ↓ ↑ ← → Exit

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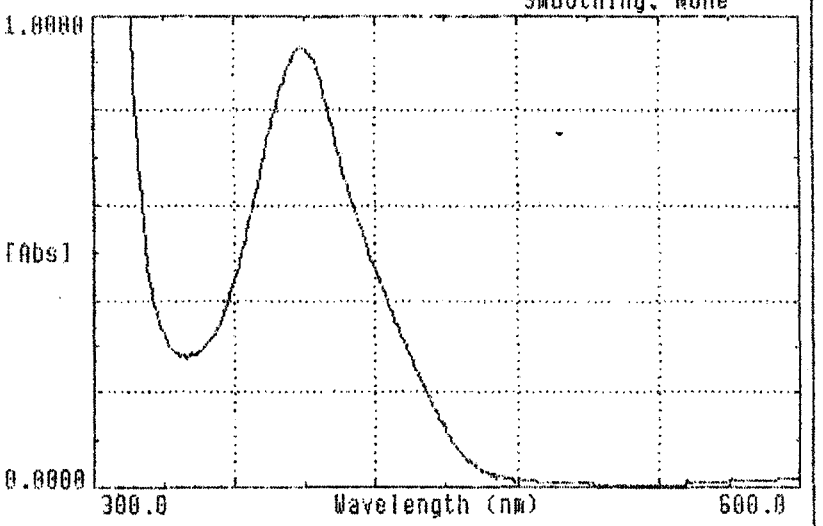
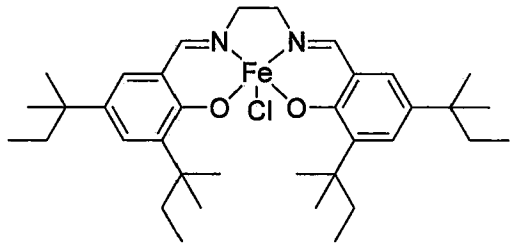


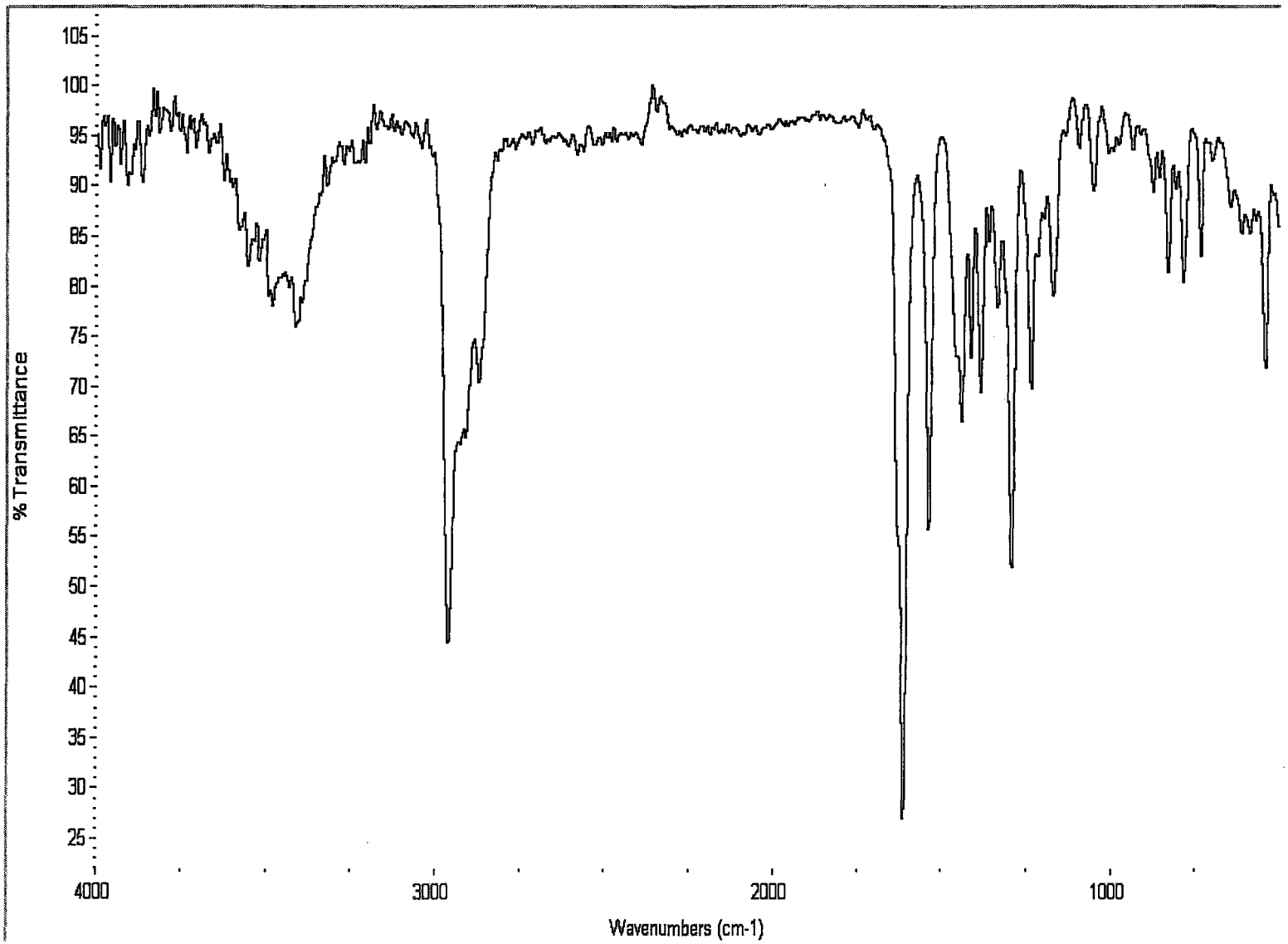
Appendix V

N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,2-ethylenediamine ferric chloride complex



(30)

FT-IR
UV
X-RAY


105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
% Transmittance
4000
3000
2000
1000
Wavenumbers (cm-1)

RCMI Facilities: Clark Atlanta Univerity

Date: 07/15/04
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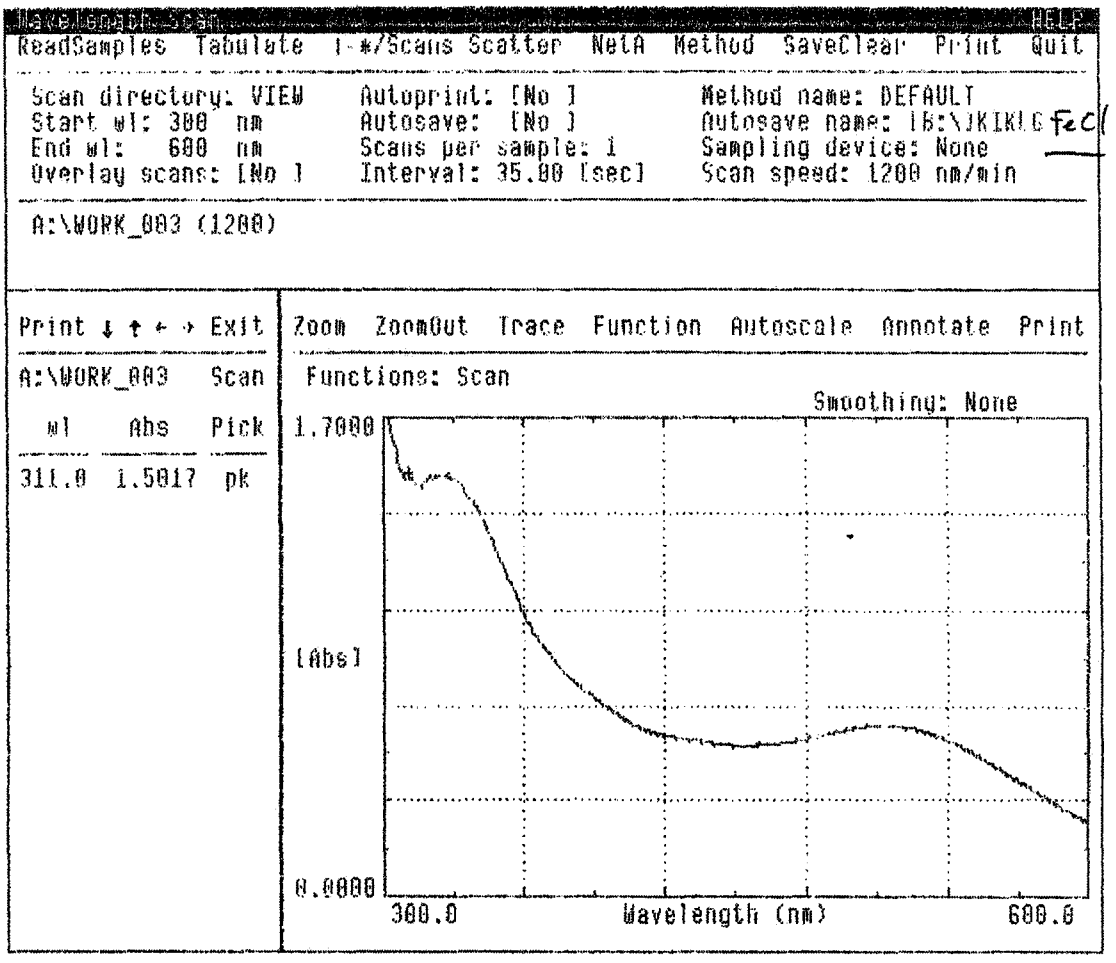

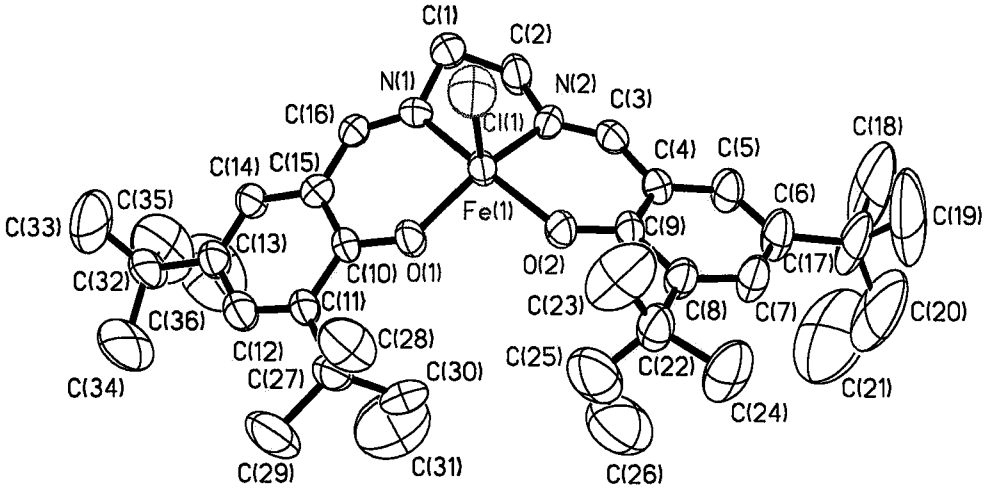
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C(2)
N(1)
N(2)
C(3)
C(16)
Cl(1)
C(4)
C(5)
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C(13)
C(10)
O(1)
O(2)
C(17)
C(32)
C(23)
C(8)
C(7)
C(20)
C(36)
C(11)
C(12)
C(28)
C(25)
C(22)
C(27)
C(30)
C(34)
C(24)
C(21)
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N,N'-Bis(3,5-di-t-pentylsalicylidene)-1,2-ethylenediamine ferric chloride complex (CIF file)

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of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc.
and is
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based
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and R-
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H3 H 0.6644 1.0640 0.1407 0.045(18) Uiso 1 1 calc R . .
C4 C 0.4604(6) 1.0834(5) 0.1616(2) 0.0406(15) Uani 1 1 d . . .
C5 C 0.4943(7) 1.1615(7) 0.1921(2) 0.056(2) Uani 1 1 d . . .
H5 H 0.5904 1.1816 0.1952 0.048(19) Uiso 1 1 calc R . .
C6 C 0.3960(9) 1.2114(7) 0.2182(3) 0.071(2) Uani 1 1 d . . .
C7 C 0.2576(8) 1.1784(7) 0.2119(3) 0.059(2) Uani 1 1 d . . .
H7 H 0.1865 1.2125 0.2295 0.036(16) Uiso 1 1 calc R . .
C8 C 0.2163(7) 1.1004(7) 0.1823(2) 0.0512(17) Uani 1 1 d . . .
C9 C 0.3227(7) 1.0482(5) 0.1563(2) 0.0412(15) Uani 1 1 d . . .
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C11 C 0.2049(7) 0.5970(6) 0.0878(2) 0.0477(15) Uani 1 1 d . . .
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C13 C 0.3547(8) 0.4622(5) 0.0540(2) 0.0517(18) Uani 1 1 d . . .
C14 C 0.4469(7) 0.5369(5) 0.0420(3) 0.0481(17) Uani 1 1 d . . .
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C15 C 0.4286(8) 0.6428(6) 0.0534(2) 0.0495(17) Uani 1 1 d . . .
C16 C 0.5356(7) 0.7138(6) 0.0424(2) 0.0458(16) Uani 1 1 d . . .
H16 H 0.6166 0.6856 0.0276 0.037(15) Uiso 1 1 calc R . .
C17 C 0.4285(10) 1.2947(11) 0.2534(4) 0.117(5) Uani 1 1 d . . .
C18 C 0.5768(13) 1.3326(16) 0.2511(7) 0.231(13) Uani 1 1 d . . .
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H19B H 0.3881 1.4234 0.2056 0.341 Uiso 1 1 calc R . .
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C20 C 0.369(2) 1.285(2) 0.2959(8) 0.228(14) Uani 1 1 d . . .
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C21 C 0.437(4) 1.185(3) 0.3164(7) 0.260(17) Uani 1 1 d . . .
H21A H 0.3804 1.1255 0.3096 0.417 Uiso 1 1 calc R . .
H21B H 0.4455 1.1930 0.3488 0.417 Uiso 1 1 calc R . .
H21C H 0.5285 1.1756 0.3034 0.417 Uiso 1 1 calc R . .
C22 C 0.0624(8) 1.0729(8) 0.1749(3) 0.071(3) Uani 1 1 d . . .
C23 C 0.0243(9) 1.0854(15) 0.1250(4) 0.125(6) Uani 1 1 d . . .
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H23B H 0.1008 1.0625 0.1064 0.200 Uiso 1 1 calc R . .
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C24 C -0.0340(8) 1.1511(10) 0.2019(4) 0.101(4) Uani 1 1 d . . .
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H24B H -0.0258 1.2198 0.1890 0.162 Uiso 1 1 calc R . .
H24C H -0.0055 1.1529 0.2333 0.162 Uiso 1 1 calc R . .
C25 C 0.0279(13) 0.9673(12) 0.1820(7) 0.132(6) Uani 1 1 d . . .
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H25B H -0.0704 0.9569 0.1775 0.211 Uiso 1 1 calc R . .
C26 C 0.0692(16) 0.9379(13) 0.2318(7) 0.155(6) Uani 1 1 d . . .
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H26B H 0.0363 0.8688 0.2386 0.249 Uiso 1 1 calc R . .
H26C H 0.0277 0.9869 0.2526 0.249 Uiso 1 1 calc R . .
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H28C H -0.0503 0.6732 0.0579 0.146 Uiso 1 1 calc R . .
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H29B H 0.0118 0.4773 0.1358 0.195 Uiso 1 1 calc R . .
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N1 0.052(3) 0.046(4) 0.054(3) -0.005(3) 0.021(3) -0.012(3)
C1 0.056(4) 0.053(5) 0.064(4) -0.012(4) 0.022(3) -0.007(4)
C2 0.054(4) 0.048(4) 0.079(5) -0.022(4) 0.011(4) -0.011(3)
C3 0.044(4) 0.041(4) 0.054(4) -0.002(3) 0.003(3) -0.010(3)
C4 0.040(3) 0.036(4) 0.046(3) -0.004(3) -0.005(3) -0.004(3)
C5 0.046(4) 0.058(5) 0.063(5) -0.025(4) -0.007(4) -0.008(4)
C6 0.061(5) 0.071(6) 0.079(5) -0.042(5) -0.008(4) -0.003(5)
C7 0.043(4) 0.065(5) 0.070(5) -0.035(4) 0.003(4) 0.000(4)
C8 0.048(4) 0.056(4) 0.050(3) -0.017(4) 0.002(3) -0.005(4)
C9 0.054(4) 0.032(3) 0.037(3) -0.005(3) -0.007(3) -0.002(3)
C10 0.049(3) 0.028(3) 0.047(3) -0.004(3) 0.002(3) -0.004(3)
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C16 0.049(4) 0.042(4) 0.047(3) -0.011(3) 0.015(3) -0.002(3)
C17 0.076(7) 0.144(12) 0.129(9) -0.112(9) 0.014(6) -0.025(7)
C18 0.098(9) 0.28(2) 0.31(2) -0.25(2) 0.017(11) -0.069(12)
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C34 0.205(14) 0.036(5) 0.202(16) 0.007(8) 0.077(13) -0.013(7)
C35 0.152(14) 0.080(9) 0.25(2) 0.006(13) 0.007(14) 0.051(10)
C36 0.171(17) 0.17(2) 0.24(2) 0.041(19) -0.091(16) 0.001(15)

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 All esds (except the esd in the dihedral angle between two l.s.
planes)
 are estimated using the full covariance matrix.  The cell esds are
taken
 into account individually in the estimation of esds in distances,
angles
 and torsion angles; correlations between esds in cell parameters are
only
 used when they are defined by crystal symmetry.  An approximate
(isotropic)
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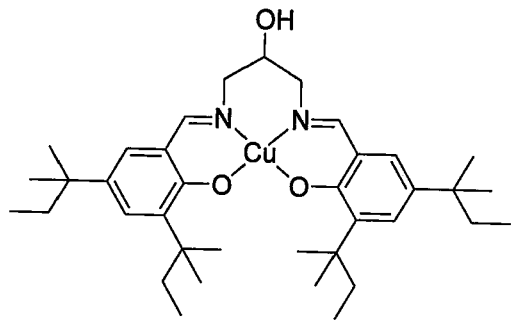
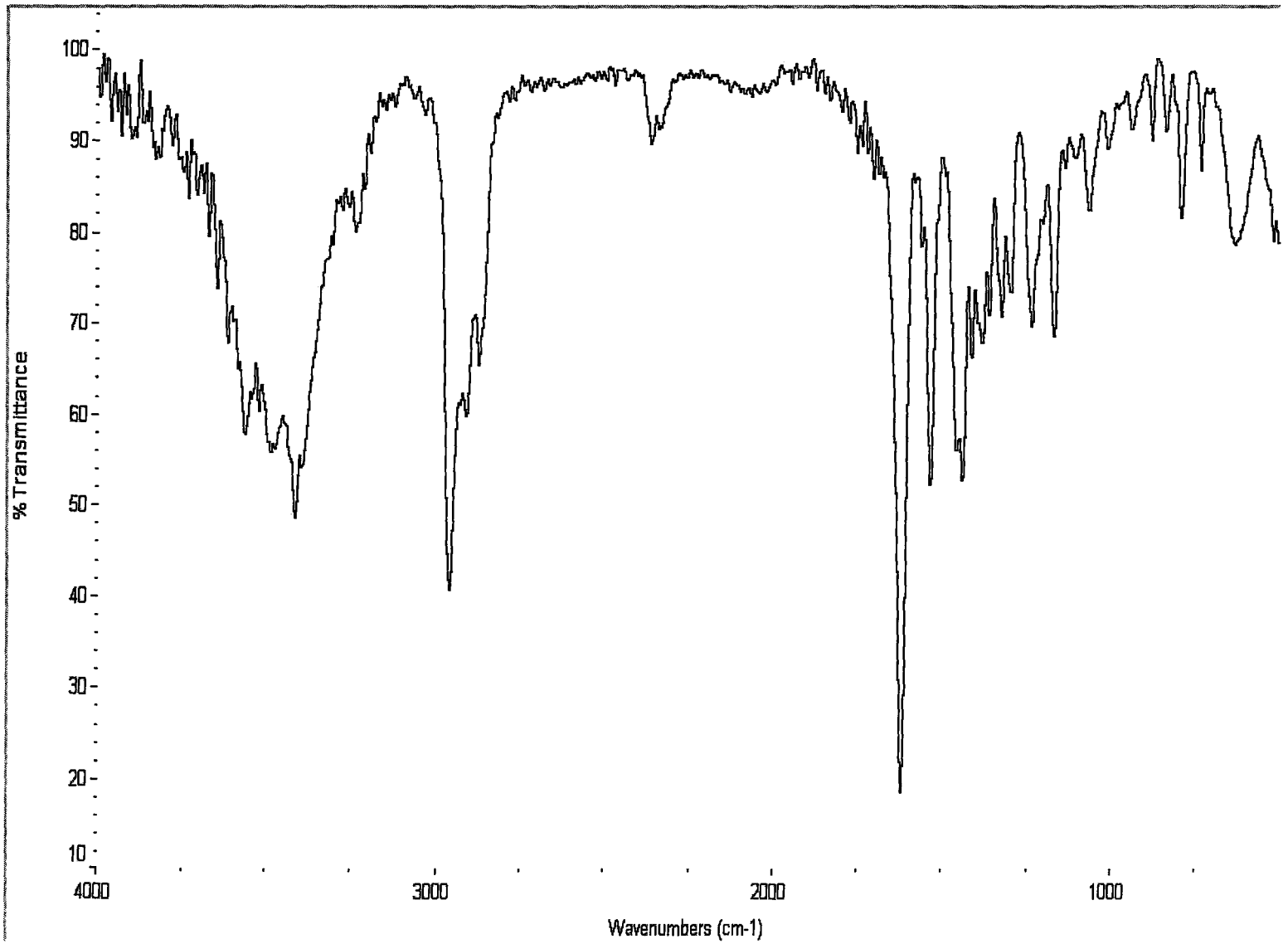
Appendix W

N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,3-diamino-propan-2-ol
copper (II) complex



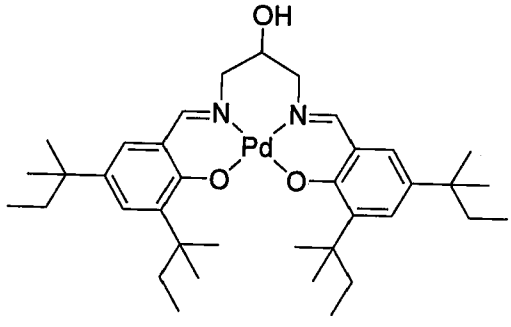
(31)

FT-IR


100
90
80
70
60
50
40
30
20
10
% Transmittance
4000
3000
2000
1000
Wavenumbers (cm-1)

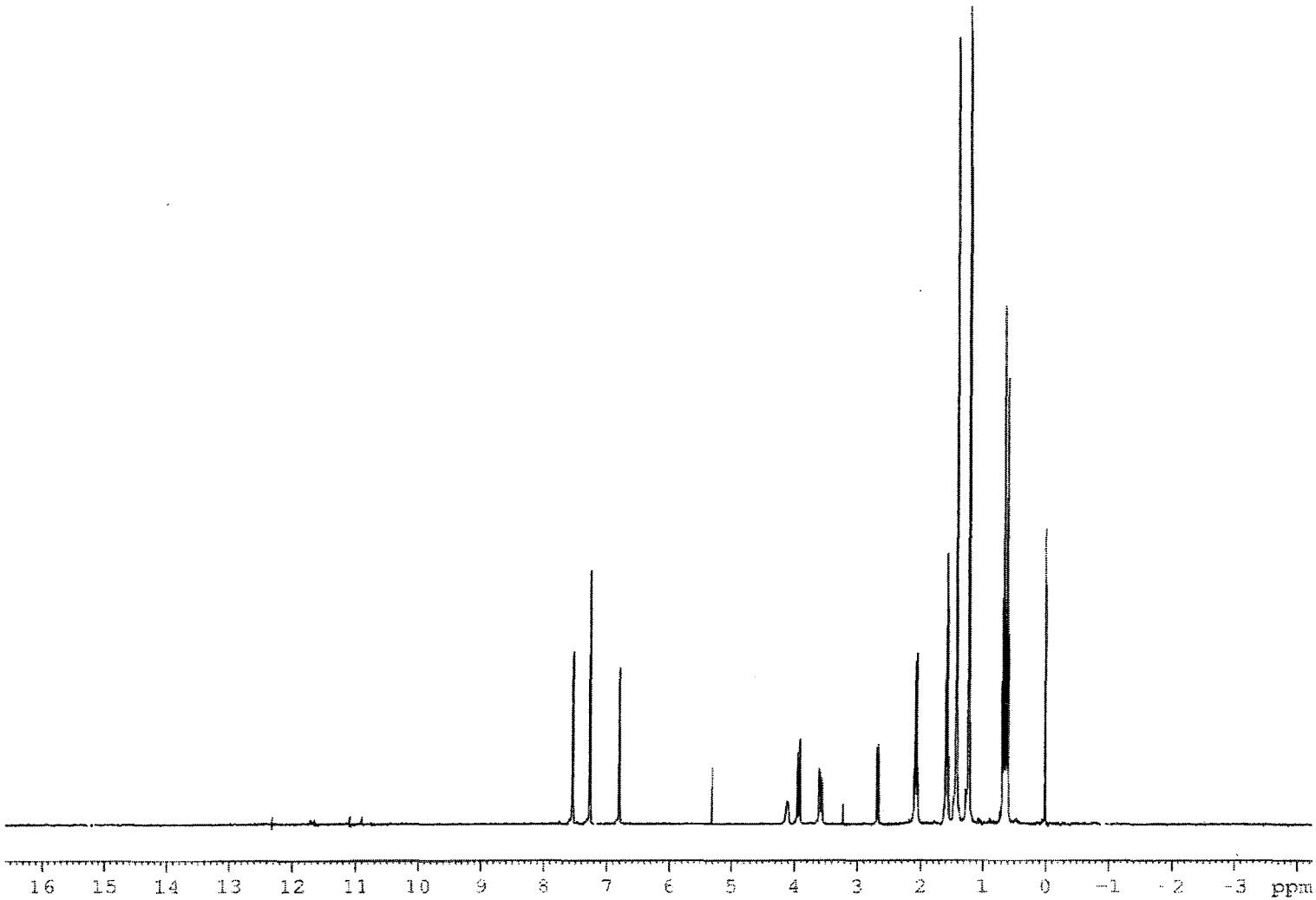
Appendix X

N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,3-diamino-propan-2-ol
palladium (II) complex

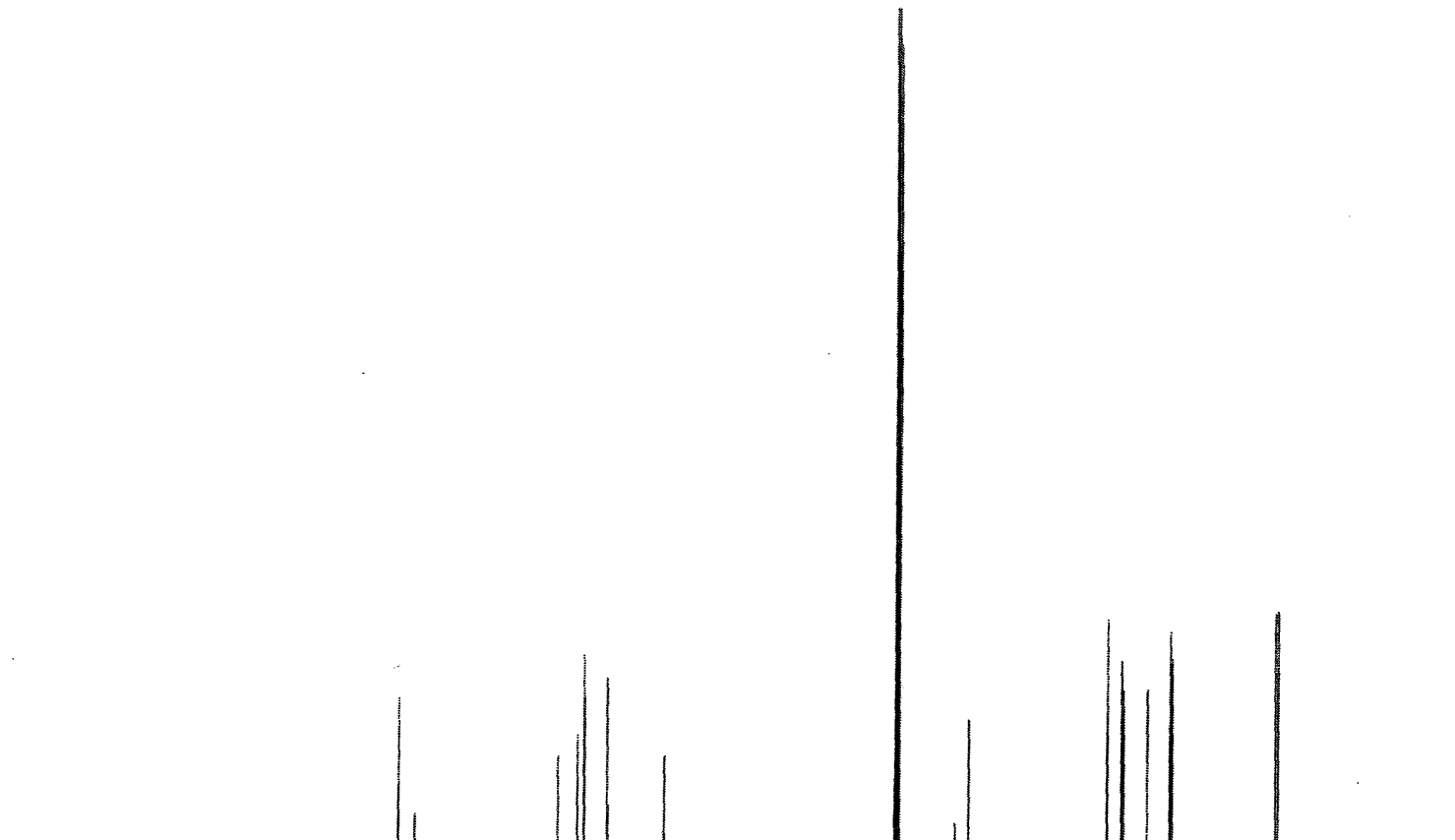


(32)

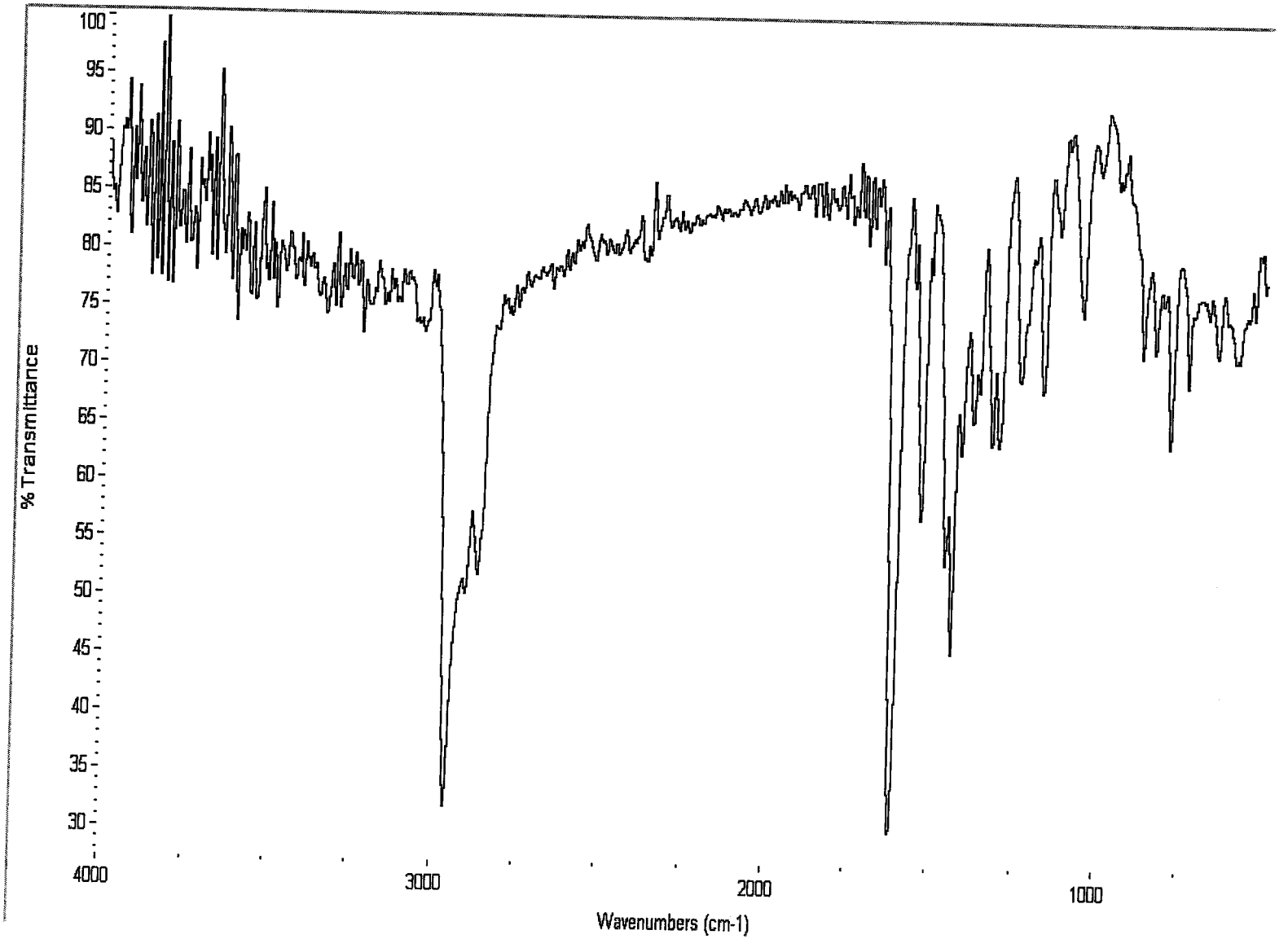
^{1}H NMR
^{13}C NMR
FT-IR



Proton NMR for N,N'-Bis(3,5-di-t-pentylsalicyldene)-1,3-diamino-propan-2-ol palladium (II) complex

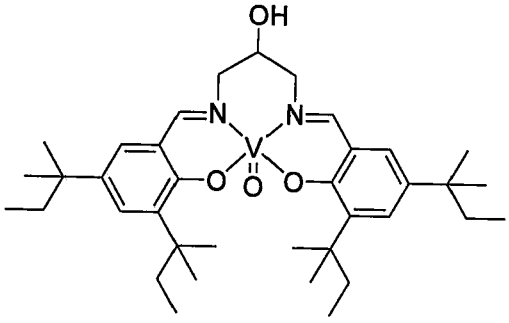


Carbon 13 NMR for N,N'-Bis(3,5-di-t-pentylsalicyldene)-1,3-diamino-propan-2-ol palladium (II) complex


100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
% Transmittance
4000
3000
2000
1000
Wavenumbers (cm-1)

Appendix Y

N,N'-Bis(3,5-di-*t*-pentylsalicylidene)-1,3-diamino-propan-2-ol
vanadyl (II) complex



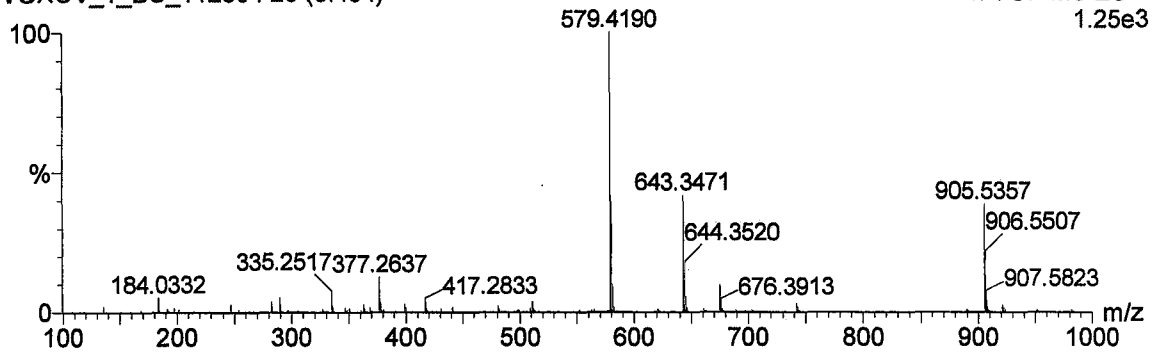
(33)

EI-MS

VOXOV, in 0.1%FA in CH3OH+CH2Cl2+, +112304 **23-Nov-2004 11:55:40**

VOXOV_1_BU_112304 26 (0.484) 1: TOF MS ES+

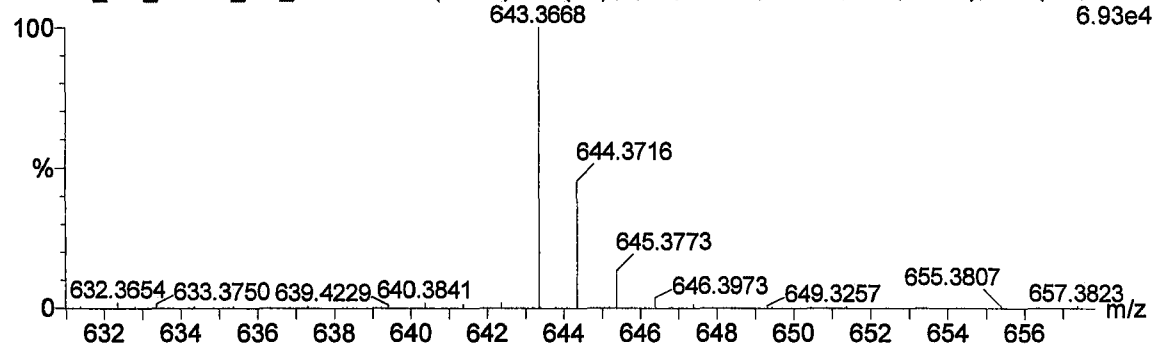
1.25e3



PVOXOV, HRMS,112304 **23-Nov-2004 12:06:36**

VOXOV_BO_HRMS_BU_112311 134 (5.048) AM (Top,4, Ar,5000.0,556.28,1.00,LS 10); Sm (Mn, 2x1.0

6.93e4



Elemental Composition Report

Single Mass Analysis (displaying only valid results)
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Even Electron Ions
1436 formula(e) evaluated with 16 results within limits (up to 50 closest results for each mass)

Minimum: -1.5

Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
643.3668	643.3667	0.1	0.2	7.5	10	C29 H51 N6 O10
	643.3666 0.2	0.3	11.5	11		C35 H54 N5 O3 51V
	643.3680 -1.2	-1.9	12.5	8		C30 H47 N10 O6
	643.3653 1.5	2.3	6.5	13		C34 H58 N O7 51V
	643.3685 -1.7	-2.6	-1.5	16		C23 H58 N7 O10 51V
	643.3648 2.0	3.1	20.5	2		C41 H47 N4 O3
	643.3688 -2.0	-3.2	24.5	7		C46 H47 N2 O
	643.3635 3.3	5.2	15.5	1		C40 H51 O7
	643.3707 -3.9	-6.0	15.5	9		C40 H54 N3 O 51V
	643.3707 -3.9	-6.0	11.5	6		C34 H51 N4 O8
	643.3626 4.2	6.5	7.5	12		C30 H54 N7 O5 51V
	643.3621 4.7	7.3	21.5	5		C37 H43 N10 O
	643.3720 -5.2	-8.1	16.5	4		C35 H47 N8 O4
	643.3613 5.5	8.6	2.5	15		C29 H58 N3 O9 51V
	643.3725 -5.7	-8.9	2.5	14		C28 H58 N5 O8 51V
	643.3608 6.0	9.3	16.5	3		C36 H47 N6 O5

REFERENCES

1. Denmark S. E.; Jacobsen E. N.; *Acc Chem. Res.* **2000**,33,324.

2. Liang S.; Bu. X. R., *J. Org. Chem* **2000**,67,2702.

3. Vandewalle, M.; Van der Eycken, J.; Oppolzer, W.; Vullioud, C. *Tetrahedron* **1986**,42,4035.

4. Morrison. J. D.: Mosher. H. S. *Asvmmetric Organic Reactions*: Prentice Hah EGelwood Cliffs, N& 1971; p 252. (b) Walborsky, H. M.; Barash, L.; Davis, T. C. *J. Org. Chem.* **1961**,26,4478.

5. Paquette, L. A. In Asymmetric Synthesis; Morrison, J. D., Ed.; *Academic Press:* New York, Vol. 3B, p 455.

6. Oppolzer, W. Angew. Chem., *Int.* Ed. Engl. **1984**, 23, 876.

7. Helmchen, *G.;* Karge, R.; Weetman, J. *In Modern Synthetic Methods* 1986;Sheffold, R., Ed.; Springer Verlag: New York, **1986**; Vol. 4, p 262.

8. Yates, P.; Eaton, P. *J.* Am. *Chem. SOC.* **1960**,82,4436.

9. Hartmann, H.; Hady, A.F.A.;Sartor,K.; Weetman, J.;Helmchen, G. Angew. *Chem., Int.* Ed. Engl. **1987**, 26, 1143.

10. Walborsky, H. M.; Barash, L.; Davis, T.C. *Tetrahedron* **1963**, 19, 2333.

11. Sauer, J.; Kredel, J. Angew. *Chem., Int. Ed Engl.* **1965**, 4, 989.

12. Hashimoto, *S.;* Komeshima, N.; Koga, K. *J. Chem. SOC.,* Chem. *Commun.* 1979,437.

13. Takemura, H.; Komeshia, M.; Takahashi, I.; Hashimoto, S.; Ikota, N.; Tomioka, K.; Koga, K. *Tetrahedron Lett.* **1987**, 28, 5687.

14. Ketter, A.; Glahsl, *G.;* Herrmann, R. *J. Chem. Res. (S)* **1990**,278-79; (M), 2118-56.

15. (a) Corey, E. J.; Imwinkelried, R.; Pikul, *S.;* Xiang, Y. B. *J. Am. Chem. SOC.* **1989**,111, 5493. (b) Corey, E. J.; Imai, N.; Pikul, *S.*

16. Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto, H. *J. Am. Chem. SOC.* **1988**, 110, 310.

17. (a) Maruoka, K.; Hoshino, Y.; Shirasaka, T.; Yamamoto, H. *Tetrahedron Lett.* **1988**, 29, 3967.

18. (a) Maruoka, K.; Banno, H.; Yamamoto, H. *J. Am. Chem. SOC.*1990, 112, 7791. (b) Maruoka, K.; Banno, H.; Yamamoto, H. *Tetrahedron: Asymmetry* 1991, 2, 647.

19. Maruoka, K.; Yamamoto, H. *J. Am. Chem. SOC.* 1989, 111, 789. Quimpere, M.; Jankowski,K. *J. Chem. SOC., Chem. Commun.* 1987,676.

20. Quimpère, M.; Jankowski, K.; *J. Chem. Soc., Chem. Commun.* **1987**, 676.

21. Narasaka, K.; Inoue, M.; Okada, *N. Chem. Lett.* 1986, 1109.

22. Champius, C.; Jurczak, *J. Helv Chim. Acta* **1987**,70, 437.

23. Seebach, D.; Beck, A. K.; Imwinkelried, R.; Roggo, *S.;* Wonnacott, A. Helu. *Chim.* Acta **1987**, 70, 954.

24. Narasaka, K.; Inoue, M.; Yamada, T. *Chem. Lett.* **1986**, 1967.

25. Narasaka, K.; Inoue, M.; Yamada, T.; Sugimori, J.; Ywasawa, *N.Chem. Lett.* **1986**, 2409.

26. Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakaehima, M.; Sugimori, J. *J. Am. Chem. SOC.* **1989**,111, 5340.

27. Reetz, M.T.; Kyung, S.H.; Bolm,C.;Zierke,T. *Chem.Ind.*(London) **1986**, 824.

28. Devine, P.; Oh, T. *J. Org. Chem.* **1991**, *57,* 396.

29. Maruoka, K.; Murse, N.; Yamamoto, H. B. *J. Org. Chem.* **1993**, *58,* 2938.

30. Posner, G.; Eydoux, F.; Lee, J.; Bull, D.; *Tetrahedron Lett.* **1994**, 35, 7541.

31. Mikami, K.; Matsukawa, S.; *Tetrahedron: Asymmetry* **1997**. 8. 815.

32. Manickam, G.; Sundararajan, G.; *Tetrahedron: Asymmetry* **1999**. 8. 2913.

33. Wang, B.; Feng, X.; Huang, Y.; Liu, H.; Cui, X.; Jiang, Y. *J. Org. Chem.* **2002**, 67, 2175.

34. Fan, Q.; Lin, L.; Liu, J.; Huang, Y.; Feng, X.; Zhang, G. *Org. lett.* **2004**, *6,* 2185.

35. Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. SOC.* **1991**, 113, 726.

36. Kelly, T. R.; Maity, S. K.; Meghani, P.; Chandrakumar, N. *S. Tetrahedron Lett.* **1989**, 30, 1357. (a) Honeychuck, R. V.; Bonnesen, P. V.; Farahi, J.; Hersh, W. H. *J. Org. Chem.* **1987**, 52, 5293.

37. Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. SOC.* **1989**, 111, 6070.

38. Olson, A. *S.;* Seitz, W. J.; Hossain, M. M. *Tetrahedron Lett.* **1991**, 32, 5299.

39. Corey, E. J.; Imai, N.; Zhang, H. Y. *J. Am. Chem. SOC.* **1991**, 113, 728.

40. Faller. J. W.: Smart. C. J. *Tetrahedron Lett.* **1989,** 30. 1189.

41. (a) Togni, A. *Organometallics* **1990**, 9, 3106. (b) Togni, A.; Pastor, *S.* T. *Chirality* **1991**, 3, 331.

42. (a) Schrauzer, G. N.; Glockner. *Chem. Ber.* **1964**, 97, 2451. (b) Lautena, M.; Crudden, C. M. *Organometallics* **1989**, 8, 2733 and references there in.

43. Lautena, M.; Lautens, J. C.; Smith, A. C. *J. Am.* Chem. *SOC.* **1990**, 112, 5627.

44. (a) Brunner, H.; Muachiol, M.; Prester, F. *Angew. Chem., Int. Ed. Engl.* 1990,29,652. (b) Brunner, H.; Prester, F. J. *Organometal.* Chem. **1991**, 414, 401.

45. Corey, E. J.; Ishihara, K. *Tetrahedron Lett.* **1992**, 33, 6807.

46. Takacs, J. M.; Lawson, E. C.; Reno, M. J.; Youngman, M. A.; Quincy, D. A. *Tetrahedron: Asymmetry* **1997**, 8, 3073.

47. Evans, D.; Shaughnessy, E. A.; Barnes, D. M.; *Tetrahedron Lett.* **1997**, 38, 3193.

48. Li, L.; Wu, Y.; Hu, Y.; Xia, L.; Wu, Y.; *Tetrahedron: Asymmetry* **1998**, 9, 2271.

49. Hu, Y.; Huang, X.; Yao, Z.; Wu, Y. *J. Org. Chem.* **1998**, 63, 2456.

50. Chapman, J. J.; Day, C. S.; Welker, M. E. *Organometallics* **2000**, 19, 1615.

51. Schaus, S. E.; Brånalt, J.; Jacobsen, E. N. *J. Org. Chem.* **1998**, 63, 403.

52. Joly, G. D.; Jacobsen, E. N. *Org. Lett.* **2002**, 4, 1795.

53. Huang, Y.; Iwana, T.; Rawal, V. H. *Org. Lett.* **2002**, 4, 1163.

54. Huang, Y.; Iwana, T.; Rawal, V. H. *J. Am.* Chem. *SOC.* **2002**, 124, 5950.

55. Bolm, C.; Simić O. *J. Am.* Chem. *SOC.* **2001**, 123, 3830.

56. De Coster, G.; Vandyck, K.; Van der Eycken, E.; Van der Eycken, J.; Elseviers, M.; Röper, H. *Tetrahedron: Asymmetry* **2002**, 13, 1673.

57. Owens, T. D.; Souers, A. J.; Ellman, J. A. *J. Org. Chem.* **2003**, 68, 3.

58. Hiroi, K.; Watanabe, K. *Tetrahedron: Asymmetry* **2002**, 13, 1841.

59. Yamamoto, Y.; Yamamoto H. *J. Am.* Chem. *SOC. Comm.* **2004**, 126, 4128.

60. K. Reimer, F. Tiemann, *Ber.* **1876, 9,** 824, 1268, 1285.

61. J. C. Duff, E. J. Bills, *J. Am. Chem. Soc.* **1932,** 1987; **1934,** 1305; **1941,** 547; **1945,** 276.

62. Casiraghi, G; Casnati, G.; Puglia, G.; Sartori, G; Terenghi, G. *J.* Chem. *SOC. Perkins I*, **1980**, 1862.

63. (a) Jaeger, F. M.; Van Dijk, J. A. *Acad. Sci. Amsterdam* **1936**, 39, 384. (b) Asperger, R. G.; Liu, C. F. *Inorg. Chem.* **1965**, 4, 1492.

64. Cashin, B.; Cunningham, D.; Daly, P.; McArdle, P.; Munroe, M.; Chonchubhair, N. Ni. *Ire. Inorganic Chemistry* **2002**, 41, 4, 773.

65. Koner, S; Iijima, S; Watanabe, M; Sato, M. *Journal of Coordination Chemistry* **2003**, 56, 103.

66. Gaquere, A.; Liang, S.; Hsu, F.; Bu, X. *Tetrahedron Lett.* **2002**, 13, 2089.